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(54) **LITHIUM-NICKEL COMPOSITE OXIDE, PROCESS FOR PREPARING THE SAME, AND POSITIVE ACTIVE MATERIAL FOR SECONDARY BATTERY**

LITHIUM-NICKEL-VERBUNDOXID, VERFAHREN ZU SEINER HERSTELLUNG UND POSITIVES AKTIVES MATERIAL FÜR SEKUNDÄRE BATTERIE

OXYDE COMPOSITE LITHIUM-NICKEL, SON PROCEDE DE PREPARATION, ET MATERIAU ACTIF POSITIF DESTINE A UNE BATTERIE SECONDAIRE

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(73) Proprietor: **FUJI CHEMICAL INDUSTRY CO., LTD.**
Nakaniikawa-gun, Toyama 930-0397 (JP)

(72) Inventors:
• **MATSUBARA, Yukio,**
Fuji Chemical Industry Co., Ltd.
Nakaniikawa-gun, Toyama 930-03 (JP)
• **UEDA, Masami, Fuji Chemical Industry Co., Ltd.**
Nakaniikawa-gun, Toyama 930-03 (JP)

• **FUKAMI, Tadashi,**
Fuji Chemical Industry Co., Ltd.
Nakaniikawa-gun, Toyama 930-03 (JP)
• **FUJIMORI, Kazumi,**
Fuji Chemical Industry Co., Ltd.
Nakaniikawa-gun, Toyama 930-03 (JP)
• **MACHI, Tamaki, Fuji Chemical Industry Co., Ltd.**
Nakaniikawa-gun, Toyama 930-03 (JP)

(74) Representative:
Weisert, Annekäte, Dipl.-Ing. Dr.-Ing.
Patentanwälte
Kraus & Weisert
Thomas-Wimmer-Ring 15
80539 München (DE)

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Description

[0001]   The present invention relates to a novel process for preparing a lithium nickel complex oxide having a high charge and discharge capacity and an excellent stability in retaining the capacity so that the degree of decrease in the capacity is little even with increasing the number of cycle, and to a positive electrode active material for a secondary battery.

[0002]   As small size electronic appliances have been rendered portable in recent years, there has been increased a demand for a lithium secondary battery having a small size, a light weight and a high energy density in place of nickel/cadmium battery.

[0003]   As active materials of positive electrode for such a lithium secondary battery, there are known $LiCoO_2$ and $LiNiO_2$ which are layered compounds capable of being intercalated and deintercalated with lithium. Of them, $LiNiO_2$ is being expected owing to its higher electric capacity than $LiCoO_2$.

[0004]   Usually, $LiNiO_2$ has been prepared by mixing a lithium component ($LiOH$, Li_2CO_3, $LiNO_3$etc.) with a nickel component (hydroxide, carbonate etc.) in a powdery form and reacting the mixture by the so-called dry process, and hence the heat at an elevated temperature for a long time was required. Especially, in the case of Ni, it is hard to convert divalent one into the trivalent one and therefore the heat at an elevated temperature for a long time was essential. Consequently, the crystal growth proceeds but some of lithium is evaporated off and NiO as a by-product is formed, thereby the lowering of the purity is caused.

[0005]   To the contrary, the present inventors succeeded previously in the preparation of highly purified $LiNiO_2$ having a high crystallization degree by forming a uniform precursor of Li and Ni components using a wet process and heating it for a short time as disclosed in Japanese Patent Application No. 6-80895 (Japanese Patent Kokai NO. 8-130013).

[0006]   As to $LiNiO_2$, however, when much Li was evaporated off (at the time of discharging), the structure tends to become unstable owing to the two dimention structure and therefore an essential problem that the cycle property of a lithium secondary battery is bad could not be overcome completely. Although the effect of improving the cycle characteristics was recognized to be achieved to some extent by using the technique of the Japanese Patent Application No. 6 - 80895 (priority application for EP-A-0 646 546), it was still insufficient in a long term cycle characteristics of more than 100 cycles.

[0007]   Under such circumstance, many attempts have been made to stabilize the structure by substituting a part of nickel for other component (third component). For example, active materials of positive electrode represented by $Li_yNi_xCo_{1-x}O_2$ (wherein x is $0 < x \leqq 0.75$ and y is $y\leqq 1$) where Co was doped as solid solution into $LiNiO_2$, and $Li_yNi_{1-x}Me_xO_2$ (wherein Me represents any one of Ti, V, Mn and Fe, x is $0< x \leqq 0.6$ and y is $0.2 < y \leqq 1.3$) where Ti, V, Mn or Fe was doped as solid solution into $LiNiO_2$ are disclosed in Japanese Patent Kokai Nos. 63-299056 and 5-283076 (corresponding to EP-A-0 554 906) respectively.

[0008]   However, the process doped third component as solid solution was carried out by a process to be said the dry process described above and hence it is difficult to dope third component as solid solution homogeneously. It involved the necessities of increasing an amount of third component, heating at an elevated temperature for a long time and conducting several times of pulverization steps inevitably. And consequently, Li was evaporated off and the by-product of NiO was formed thereby the lowering of the purity was caused and and sufficient improvement in cycle property could not be achieved like $LiNiO_2$ described above. Also, since the dry process required a long term heat and pulverization steps it was bad in the production efficiency and uneconomical. Furthermore, as it takes a long time for the heating inevitably in these dry processes, it was impossible to adjust crystal size to a desired, keeping a crystallization degree and purity at high level.

[0009]   Under these circumstances, some attempts have been made to prepare spherical particles for increasing a packing density. For example, a technique is disclosed in Japanese Patent Kokai No. 7-105950 for preparing spherical $LiNiO_2$ particles having 5 μm $\sim$ 50 μm using spherical $Ni(OH)_2$. This technique is one for obtaining spherical $LiNiO_2$ using spherical $Ni(OH)_2$ as raw material by a dry process for the purpose of increasing a packing density only. But, the primary particle size and the purity of $LiNiO_2$ was not taken into consideration. The result was not satisfactory. Another technique is disclosed in Japanese Patent Kokai No. 6-333562 for preparing spherical $LiNiO_2$ having 0.1$\sim$ 1.1 μm with a mist dry process. In this technique, the crystal size is too fine so that the crystals are passed through a sepalator when employed as a battery and thus it is not practical for battery use. Especially in case of $LiNiO_2$, when the primary particles are too fine there is caused a problem that the storage stability is poor owing to moisture absorption so that good and stable battery characteristics cannot be obtained.

[0010]   Moreover, it is known that when the battery was once placed under an elevated temperature, for example in a car in the daytime, even if it was reverted to the normal temperature, the positive electrode active material is susceptible to deterioration to a great extent and discharge performance becomes bad so that the battery performance is decreased greatly.

[0011]   As the means to prevent the deterioration of the positive electrode active material, in considering the fact that finer the primary particle size, has greater the deterioration, how large is the primary particle size of the active material

to be prepared has been noticed.

[0012] As a process for improving the storage stability or the discharge characteristics of the positive electrode active material at high temperature by making the primary particle size large, there have been reported with respect to $LiCoO_2$ series some attempts to make the primary particle size large by improving the heating condition [Japanese Patent Kokai No. 6-243897 (0.1 $\sim$ 2.0 µm), Japanese Patent Kokai No. 6-325791(0.01 $\sim$ 5 µm) and Japanese Patent Kokai No. 7-14579 (0.01 $\sim$ 5 µm)].

[0013] Also, the primary particle having an average size of higher than 2 µm is prepared by adding Bi oxide to the raw material resource as proposed in Japanese Patent KoKai No. 8-55624. Thus it is easy for $LiCoO_2$ series to make the primary particle size large.

[0014] On the other hand, there has not been found yet any example of having made the primary particle of $LiNiO_2$ such large as seen in $LiCoO_2$ series. The reason is attributed to that the synthesis of $LiNiO_2$ or third component (M) added related compound $Li_yNi_{1-x}M_xO_2$ required the heating at an elevated temperature for a long time owing to their bad reactivity as described above, thereby Li is liable to be evaporaled off. And consequently the crystal growth is hard to proceed and becomes imperfect crystals having much lattice defect. For this reason, the heating has been conducted at possible high temperature within the permissible temperature range and as a result only fine primary particle of less than 1µm could be obtained.

Disclosure of The Invention

[0015] The objects of the present invention are to provide (1) a novel process for preparing a lithium nickel complex oxide wherein the crystals have been developed sufficiently and are highly purified and whoes stability of a high charge and discharge capacity is excellent ; by said process the size and shape of said lithium nickel complex oxide may be set to desired one and (2) a positive electrode active material for a secondary battery containing as an effective component this complex oxide.

[0016] That is, the present invention relates to a process for preparing a lithium nickel complex oxide which is represented by the general formula (I) :

$$Li_{y-x1}Ni_{1-x2}M_xO_2 \qquad\qquad (I)$$

wherein M represents a metal selected from the group consisting of Al, Fe, Co, Mn and Mg, $x = x_1 + x_2$ and

(i) when M is Al or Fe, then x, x_1 and x_2 represent respectively $0 < x \leq 0.2$, $x_1 = 0$, and $x_2 = x$;
(ii) when M is Co or Mn, then x, x_1 and x_2 represent respectively $0 < x < 0.5$, $x_1 = 0$, and $x_2 = x$;
(iii) when M is Mg, then x, x_1 and x_2 represent respectively $0 < x < 0.2$, $0 < x_1 \leq 0.2$ and $0 < x_2 \leq 0.2$; and y represents $0.9 \leq y < 1.3$,

said process comprising the steps of :

(a) reacting a basic metal salt represented by the general formula (II)

$$Ni_{1-x}M^p{}_x(OH)_{2-nz}(A^{n-})_{[Z+(px-2x)/n]} \cdot mH_2O \qquad\qquad (II)$$

wherein M represents a metal selected from the group consisting. of Al, Fe, Co, Mn and Mg, p is a valence number of M with $2 \leq p \leq 3$, A^{n-} is an anion having a valence of n, and x, z and m are positive numbers respectively satisfying the ranges of $0 < x \leq 0.2$, $0.03 \leq z \leq 0.3$, $0 \leq m < 2$; with a water soluble lithium compound in an aqueous medium in a molar ratio of Li/(Ni+M) of 0.9 $\sim$ 1.3 to obtain a slurry,
(b) spray drying the obtained slurry; and
(c) heating the resultant dry material at a temperature of about 600°C $\sim$ 900°C for about 4 hours or more in an oxidative atmosphere.

[0017] The lithium nickel complex oxide represented by the above general formula obtained by the process of the present invention may be more specifically classified into ones shown by the following general formulae (I a) $\sim$ (I c):

[0018] A lithium nickel complex oxide represented by the formula (Ia):

$$Li_yNi_{1-x}M_xO_2 \tag{Ia}$$
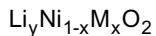
(wherein M represents Al or Fe, x, x_1 and x_2 represent respectively $0 < x \leqq 0.2$, x1 = 0, and $x_2 = x$) is one wherein a small amount of Al or Fe has been uniformly doped as the solid solution in the trivalent form thereby the structure is stabilized and cycle characteristics is enhanced whereas any battery characteristics cannot be achieved even when Al or Fe was converted into the corresponding $LiMO_2$.

[0019] If x is less than 0.01, it is not preferable because the amount doped of Al or Fe as the solid solution is little so that the stabilization of the structure is insufficient and the cycle property becomes bad. Also, when x exceeds 0.2, the doping is insufficent and the impurities are formed so that discharge capacity decreases rapidly and the desired high capacity is lost which is an essential function for the positive electrode active material for a lithium secondary battery in the present invention.

[0020] A lithium nickel complex oxide represented by the formula (I b):

$$Li_yNi_{1-x}M_xO_2 \tag{Ib}$$

(wherein M represents Co or Mn, x, x_1 and x_2 represent respectively $0 < x \leqq 0.5$ x1 = 0, and $x_2 = x$) is one wherein Co or Mn has been doped as the solid solution in relatively large amount thereby the structure is stabilized and a high electric capacity is retained although the battery characteristics can also be achieved when Co or Mn was converted into $LiMO_2$.

[0021] If x is less than 0.01, it is not preferable because the amount doped of Co or Mn is little and the stabilization of the structure is insufficient. When x exceeds 0.5, in the case of Co, the amount doped is much thereby not only discharge capacity is decreased but also it is not advantageous economocally because of a large amount of an expensive cobalt to be intercalated. Also, in the case of Mn, inherently discharge capacity is small. When x exceeds 0.5, the desired high capacity is lost which is an essntial function for the positive electrode active material for a lithium secondary battery in the present invention.

[0022] A lithium nickel complex oxide represented by the following formula (I c) where M is Mg in the formula (I)

$$Li_{y-x1}Ni_{1-x2}Mg_xO_2 \tag{Ic}$$
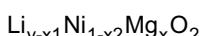
(wherein x, x_1 and x_2, x represent respectively $0 < x \leqq 0.2$, $0 < x_1 < 0.2$, and $0 < x_2 < 0.2$ and y represents $0.9 \leqq y \leqq 1.3$) is one wherein Mg which itself has no electric characteristics has been uniformly and partially doped as the solid solution into each of Li and Ni layers thereby the structure is stabilized and the cycle characteristics is enhanced.

[0023] If x is less than 0.01, it is not preferable because the amount doped of Mg is little and the stabilization of the structure is insufficient. When x exceeds 0.2, the doping is insufficient and the impurities are formed so that discharge capacity decreases rapidly and the desired high capacity is lost which is an essential function of the positive electrode active material for a lithium secondary battery in the present inventiion.

[0024] The above -mentioned lithium nickel complex oxide prepared by the process of the present invention is composed of spherical particle to be formed by a wet-spray dry processes as described later and large primary particle size to be formed by the subsequent press process wherein the spray dried product (spherical particle product) is employed as raw material for heating as described later.

[0025] First, the lithium nickel complex oxide prepared by the process of the present invention will be illustrated with respect to spherical particle one formed by spray dry process. The spherical particle has characteristic properties as shown below.

[0026] The first feature is that the purity is high so that any impurities cannot be detected by a X - ray diffractometry. And, a ratio in peak intensity of the face (003) to the face (104) of Miller indices hkl of the X-ray diffraction pattern i.e., (003)/(104) is 1.2 or higher and a ratio in the peak intensity of the face (006) to the face (101) i.e., (006)/(101) is 0.13 or lower, and the proportion of Ni^{3+} to the total Ni is 99 % by weight or higher, thus it is highly prified. Usually the stability of the structure is enhanced by the substitution of a part of Ni for other component (third component) but the purity decreases relative to the substitution amount.

[0027] In spite of the substitution of Al, Fe, Mg, Co or Mn having been done in the present invention, highly purifird complex oxide may be obtained. That is, Al or Fe which is third component takes trivalence in the structure so that the structural unstability of Ni by reversibly deintercalation of Li can be solved. In the case of Mg, it is intercalated into each part of lithium and nickel layers thereby the structural instability is avoidable. With respect to Co or Mn, each of them has been uniformly doped whereby the structural unstability of Ni by reversibly deintercalation of Li can be solved. The

most important feature of the lithium nickel complex oxide prepared by the process of the present invention lies in that one of these third components are doped uniformly and in a very small amount not so as to exceed the required amount.

[0028] This has a close relation with a process to be said an aqueous solution process (wet process) as described later as well as size of the primary particles as described later. The complex oxide is essentially composed of the primary particles having a specific size thereby there can be obtained composition which has a high purity and a high crystallization degree and which is stable in quality.

[0029] The second feature lies in that the complex oxide is composed of the primary particles which are uniform particles which is distributed in the range of 0.2 ~ 3.0 μm in terms of the long diameter with the average diameter of 0.3 ~ 2.0 μm as observed with a SEM.

[0030] In general, the size of the primary particle is important for a layered compound represented by $LiMO_2$ in the light of the reversibly de - intercalation of Li. Finer the primary particles, better ionic conductivity in the inside of the solid and Li is more reversibly de-intercalatable with the outside.

[0031] On the other hand, in regard of the crystallization degree if the primary particle is 0.2 μm or less the crystal growth does not proceeds sufficiently and the purity becomes low inevitably. Also, if it is 0.2 μm or less, then the storage stability is poor owing to moisture absorpbility and so good battery characteristics cannot be achieved stably. Moreover, in considering that quality is stable it is desirable that the the size of the primary particle is uniform.

[0032] As a result of having studied ardently about the primary paticle size from the above viewpoints, the present inventors have found that the primary particles in the lithium nickel complex oxide prepared by the process of the present invention have the desirable performance when they are uniform particles which are distributed in the range of 0.2~ 3.0 μm in terms of the long diameter with the average diameter of 0.3 ~ 2.0 μm, preferably 0.3 ~ 1.0 μm, as observed with a SEM.

[0033] Third feature is that the secondary particles are made into spherical shape by wet-spray dry processes as described later and the average size of the secondary particles D lies in the range of 5 ~ 100 μm with 10 % of the particle size distribution being 0.5D or higher and 90 % 2D or lower, and the surface is in uneven state as can be seen under observation of a SEM.

[0034] Also, the particle ratio (a ratio of the long diameter to the short diameter) of the spherical secondary particles as observed with a SEM lies in the range of a maximum of 1.5 or less and an average of 1.2 or less with 90 % or more of them being distributed in 1.3 or less, indicating that they are uniform particles even when there was included some of slightly larger particle ratio than one defined above in the complex oxide prepared during pulverization after the heating has been conducted.

[0035] It is understood from such physical properties that not only they are suitable for the closest packing density but also they have an advantage when used as battery that the contact surface with each of an electrolyte and a conductive agent becomes large so it is easy to de-intercalate Li.

[0036] The size of the spherical secondary particles can be set to the range of from 5μ m to 100 μm as desired. However, an average size of about 5 ~ 30 μm m is desirable for use as the battery material from the viewpoint of processbility. Also, the BET specific surface area lies in the range of 0.1 ~ 2 m^2/g. When used as the battery material, since there is no increase in the viscosity of an electrolyte the lowering of conductivity does not be caused.

[0037] The lithium nickel complex oxide represented by the general formula (I) in the present invention is prepared by the process as described above.

[0038] As the water soluble lithium compound and the basic metal salt, there may be employed one each containing an anion which is evaporated off during the heating.

[0039] As the lithium compound, there may be selected one or more from among LiOH, $LiNO_3$, Li_2CO_3 and hydrates thereof.

[0040] In the basic metal salt represented by the above general formula (II) as an example of A^{n-} there may be selected from compounds shown by NO_3^- , Cl^-, Br^-, CH_3COO^-, CO_3^{2-} and SO_4^{2-}.

[0041] In the above general formula (II), when M is Al or Fe, p in M^p is trivalence, thereby forming hydrotalcite compounds (in the case of Fe, a part of divalent one may be contained and it causes no problem since it converts easily into trivalent one during the reaction with a lithim compound and the drying step). When M is Co or Mn, p may be divalence, trivalence or mixture thereof since it may be used equally without problem. When M is Mg, p is divalent.

[0042] Among these compounds, LiOH is preferred as the lithium compound and a basic metal nitrate where A^{n-} is NO_3^- is preferred as the basic metal salt represented by the general formula (II), from the viewpoint of yield, reactivity, effective utilization of the resources and oxidation accelerating effect. This combination is particularly preferred from the viewpoint of battery characteritics.

[0043] It is recommended from the viewpoint of uniformity that the basic metal salt is in fine particles of 0.1 μm or less with respect to the crystallite of the primary particle as measured by the Scherrer's method.

[0044] Also, it is preferred from the viewpoint of surface reactivity that this fine particle has a BET specific surface area of 10m^2/g or higher, preferably 40 m^2/g or higher, more preferably 100 m^2/g or higher. As to the BET specific surface area, if it is measured after an aqueous solution of a basic metal salt has been dried, then the primary particles

of very fine particles aggregates during dry process, thus BET specific surface area measured is one for the aggregation. If aggregate is strong, nitrogen gas cannot enter into it so that the value of BET specific surface area becomes small. Accordingly the basic metal salt which is practically reacted with a lithium compound in aqueous solution shows a high BET specific surface area to exhibit that the surface has a high reactivity. However, BET specific surface area was set to $10 m^2/g$ or higher from the above actual circumstances. This basic metal salt having the specific composition has a layered structure, and both the chemical composition and the crystal structure are similar to those of $Ni_{1-x}M_x$ $(OH)_2$. Moreover, it is microcrystalline and the surface is highly active as described above, so that it is reacted with a lithium compound such as LiOH thereby forming an extremely desirable precursor of $Li_{y-x1}Ni_{1-x2}M_xO_2$.

[0045] Highly purified $Li_{y-x1}Ni_{1-x2}M_xO_2$ having an extremely high crystallization degree is obtained only when such a basic metal salt having a specific composition is used. The $Ni_{1-x}M_x(OH)_2$ is inferior in the reactivity with the lithium compound to the basic metal salt. On the other hand, when the amount of an anion is increased, the structure of the basic metal salt is increasingly deviated from the layered structure, and the anion inhibitively acts on the formation $Li_{y-x1}Ni_{1-x2}M_xO_2$ during the heating, so that the desired compound having a high purity and an extremely high crystallization degree cannot be obtained.

[0046] The basic metal salt to be used in the process of the present invention can be prepared by adding an alkali to an aqueous solution of $Ni_{1-x}M_x$ salt in an amount of about 0.7 ~ 0.95 equivalent, preferably about 0.8 ~ 0.95 equivalent based on the $Ni_{1-x}M_x$ salt and reacting at atemperature of about 80°C or lower. Examples of the alkalis to be used in the reaction include alkali metal hydroxides such as sodium hydroxide, alkaline earth metal hydroxides such as calcium hydroxide, amines and the like. In this connection, it is preferable that, after the preparation, this basic metal salt be matured at 20 ~ 70°C for 0.1 ~ 10 hours. Subsequently, any by-products are removed by washing with water and the lithium compound is added.

[0047] The drying of the slurry obtained by such a reaction is carried out by spray drying. The spray drying where drying can be instantaneously accomplished to obtain spherical particles is preferred from the viewpoint of spherical particle granulation and the uniformity of the composition (In such dry processes requiring a certain drying time as shelf type drying and band drying ones, some Li migrates into the surface of particles to result in non - uniform composition).

[0048] In case that spherical particles with uniform composition obtained using wet and spray drying processes is subjected to the heating as it is, the heating is effected at a temperature of 600°C ~ 800°C, preferably 700°C ~ 750°C for 4 hours or higher, preferably about 4 ~ 20 hours in an atmosphere of oxygen. If the heating time is more than 20 hours, not only it makes cost up but also it causes evaporation of Li thereby the proportion of trivalent Ni to the total Ni becomes rather low and so the purity becomes bad.

[0049] In the known technique by the drying process regarding the heating, both the Li and Ni components are non-uniform in any cases during the reaction where the divalent Ni is converted into trivalent Ni, and hence the heating of at least 20 hours was required for Ni which is hard to become trivalent. In the light of the fact, the process of the present invention wherein an uniform spray dried powdered product is heated as it is is very economical and advantageous.

[0050] Nextly, the process for preparing the complex oxide having large primary particles and a positive electrode active material for a secondary battery which contains as an effective ingredient said complex oxide will be illustrated more specifically.

[0051] An average long diameter of this large primary particle product is a range of 1 ~ 10 μm.

[0052] By using the spherical particle product obtained by the above -mentioned spray drying process as a positive electrode active material for a secondary battery and setting properly the kind of a metal as third component and the amount to be doped as solid solution, remarkable improvement in cycle characteristics may be achieved sufficiently, retaining the desired battery capacity. However, the recognition regarding the safety is being requested in the public. As to the battery to be used practically there has been increased the discussion that the use of it under severe conditions in a very rare case should be taken into consideration. Under the present situation where the function for the safety as a composite battery including other battery materials (native electrode, an electrolyte, sepalator etc.) with a positive electrode active material is not matured yet, a positive electrode active material which can be used at an elevated temperature has been required strongly.

[0053] The present invention has been made to meet this requirement and provide a positive electrode active material having the following characteristic properties.

[0054] That is, the composition of the positive electrode active material is similar to that of the above spherical particle product and the characteristic properties is characterized by that a ratio in peak intensity of the face (003) to the face (104) of Miller indices hkl of the X-ray diffraction pattern i.e., (003)/(104) is 1.2 or higher and a ratio in the peak intensity of the face (006) to the face (101) i.e., (006)/(101) is 0.13 or lower, and an average long diameter of the primary particle product is a range of 1 ~ 10 μm, more preferably 2 ~ 10 μm, as measures with a SEM.

[0055] Said lithium nickel complex oxide prepared by the process of the invention is one wherein an average long diameter of the primary particles in the sufficiently developed crystals is large and which are excellent in stability.

[0056] Also, it is preferable that the positive electrode active material having large primary particles is highly purified

to such extent as the proportion of Ni^{+3} to the total Ni is 99 % by weight or higher like the spray dried particle product described above. It should have a BET specific surface area of $0.01 \sim 1 \, m^2/g$, thus it has adversely small BET specific surface area to that extent that particles became larger. When used as the battery material, it does not cause any raise in the viscosity of the electrolyte and the reactivity with the electrolyte is small.

[0057]   The lithium nickel complex oxide having a large primary particle is obtained by reacting a basic metal salt represented by the above-mentioned general formula (II) as the starting material with a water soluble lithium compound in an aqueous medium under condition such that a molar ratio of Li / (Ni + M) becomes $0.9 \sim 1.3$, spray drying the obtained slurry, and subjecting the spray dried product to press molding.

[0058]   As the process for preparing the positive electrode active material, there may be applied one wherein the spray dried product is subjected to press molding and then the heating is conducted and an alternative one wherein after the spray dried product has been once heated as it is, resultant heat-treated product is subjected to press molding and then re-heating is conducted.

[0059]   First process is one which comprises subjecting the spray dried product to press molding and then firing the resultant molded material at a temperature of about $600°C \sim 900°C$ for about 4 hours or more in an oxidative atmosphere.

[0060]   The spherical particle product obtained by the above-mentioned spray dried process of the present invention is excellent in flowability, molding and filling properties, and may be pressed into a shape as it is according to the conventional manner, for example under a static pressure of usually $500 \sim 3,000 \, kg \, /cm^2$, preferably $800 \sim 1,500 \, kg/cm^2$ using a Brinell hardness tester. The press molding is of a great significance in that moving distance among molecules becomes short and thereby the crystal growth during the firing is accelerated.

[0061]   The press molded product obtained thusly can be heated as it is.

[0062]   The heating is effected at a temperature of usually $600 \sim 900°C$, preferably $750°C \sim 800°C$ for a period of usually 4 hours or higher, preferably $10 \sim 72$ hours under an atmosphere of oxygen.

[0063]   The crystal growth of primary particles during the heating is accelerated by a press molding and thereby obtaining the complex oxide having larger primary particles.

[0064]   The process wherein this spherical particle product is hired through the press molding makes it possible to prepare a complex oxide having a high purity and a high crystallization degree even when the heating time of more than 20 hours was taken unlike the process wherein the spherical particle product is heated as it is for the reason that the contact area between particles becomes small because of compressed material so that evaporation of Li and formation of by-product NiO do not occur.

[0065]   Second process for preparing the desired complex oxide is one wherein the spray dried product is heated at a temperature of $600°C \sim 900°C$ for 0.5 hour or more under an atmosphere of oxygen, the obtained heat-treated product after pulverized if necessary is pressed into a shape in a similar manner as in the first process, and then re - heated at a temperature of $600°C \sim 900°C$ for 1 hour or more under an atmosphere of oxygen, This process has an advantage that the total time requird for the heated process may be shortened in comparison with the first process. In this connction, even when the spherical particle product which may be obtained by the above - mentioned spray drying process was heated for a long time as it was, the primary particles become large no longer. The heat-treatment for 20 hours gives the average particle size of $2\mu m$ or less while the heat- treatment for 72 hours gives the average particle size of about $2 \sim 3 \, \mu m$ or less.

[0066]   Also, even when the press molding process was applied to the powdered complex oxide obtained by the prior art drying process, the average particle size of the 20 hours heated product is $1 \, \mu m$ or less, and there is almost no appreciable change in the particle size even when the heating time was merely extended further as shown in Comparative Examples described later.

[0067]   Therefore, the combined process of the wet, spray drying and press molding ones involved in the present invention is extremely advantageous in making the primary particle larger.

[0068]   In addition, although a distinct cause why it occurs has not been clear yet, the moving distance between powder-powder and that between Li and Ni molecules are considered to be decreased by the pressing procedure according to the present process, so that the evaporation of Li and formation of the by-product NiO may be suppressed and the desired complex oxide having a high purity and a high crystallization can be obtained even when the heat process was conducted for a long time.

[0069]   As is apparent from the Examples described later, the complex oxide having larger primary particle is poor in the reactivity and has a small battery capacity owing to the larger primary particle but the stability (cycle property and high temperature stabilities) is enhansed to that extent.

[0070]   The heat - treated product composed of lithium nickel complex oxide obtained thusly may be properly pulverized into the desired size depending on use.

[0071]   As is apparent from the Examples and Comparative Examples described later, when the lithium nickel complex oxide prepared by the process of the present invention is used as a positive electrode active material for a secondary battery, high discharge capacity of $130 \sim 200 \, mAh/g$ may be achieved and the decrease rate in discharge capacity is

less than 10 % even after 100 cycles,indicating that it can be effectively utilized because of stablility.

Brief Description of the Drawings

[0072]   Fig. 1 is X-ray diffraction pattern (XRD) of the complex oxide obtained in Example 1.
[0073]   Fig. 2 is SEM photograph (150 magnifications) of the complex oxide obtained in Example 1.
[0074]   Fig. 3 is SEM photograph (30,000 magnifications) of the complex oxide obtained in Example 1.
[0075]   Fig. 4 is particle size distribution of the complex oxide obtained in Example 1.
[0076]   Fig. 5 is XRD of the complex oxide obtained in Example 5.
[0077]   Fig. 6 is SEM photograph (10,000 magnifications) of the complex oxide obtained in Example 5.
[0078]   Fig. 7 is XRD of the complex oxide obtained in Example 6.
[0079]   Fig. 8 is SEM photograph (150 magnifications) of the complex oxide obtained in Example 6.
[0080]   Fig. 9 is SEM photograph (30,000 magnifications) of the complex oxide obtained in Example 6.
[0081]   Fig. 10 is particle size distribution of the complex oxide obtained in Example 6.
[0082]   Fig. 11 is XRD of the complex oxide obtained in Example 9.
[0083]   Fig. 12 is SEM photograph (10,000 magnifications) of the complex oxide obtained in Example 9.
[0084]   Fig. 13 is XRD of the complex oxide obtained in Example 10.
[0085]   Fig. 14 is SEM photograph (30,000 magnifications) of the complex oxide obtained in Example 10.
[0086]   Fig. 15 is particle size distribution of the complex oxide obtained in Example 10.
[0087]   Fig. 16 is XRD of the complex oxide obtained in Example 13.
[0088]   Fig. 17 is SEM photograph (10,000 magnifications) of the complex oxide obtained in Example 13.
[0089]   Fig. 18 is XRD of the complex oxide obtained in Example 14.
[0090]   Fig. 19 is SEM photograph (150 magnifications) of the complex oxide obtained in Example 14.
[0091]   Fig. 20 is SEM photograph (10,000 magnifications) of the complex oxide obtained in Example 14.
[0092]   Fig. 21 is particle size distribution of the complex oxide obtained in Example 14.
[0093]   Fig. 22 is XRD of the complex oxide obtained in Example 16.
[0094]   Fig. 23 is SEM photograph (1,000 magnifications) of the complex oxide obtained in Example 16.
[0095]   Fig. 24 is SEM photograph (10,000 magnifications) of the complex oxide obtained in Example 16.
[0096]   Fig. 25 is particle size distribution of the complex oxide obtained in Example 16.
[0097]   Fig. 26 is XRD of the complex oxide obtained in Example 19.
[0098]   Fig. 27 is SEM photograph (10,000 magnifications) of the complex oxide obtained in Example 19.
[0099]   Fig. 28 is XRD of the complex oxide obtained in Example 21.
[0100]   Fig. 29 is SEM photograph (50 magnifications) of the complex oxide obtained in Example 21.
[0101]   Fig. 30 is SEM photograph (30,000 magnifications) of the complex oxide obtained in Example 21.
[0102]   Fig. 31 is particle size distribution of the complex oxide obtained in Example 21.
[0103]   Fig. 32 is XRD of the complex oxide obtained in Comparative Example 1.
[0104]   Fig. 33 is SEM photograph (1,000 magnifications) of the complex oxide obtained in Comparative Example 1.
[0105]   Fig. 34 is SEM photograph (10,000 magnifications) of the complex oxide obtained in Comparative Example 1.
[0106]   Fig. 35 is particle size distribution of the complex oxide obtained in Comparative Example 1.
[0107]   Fig. 36 is XRD of the complex oxide obtained in Comparative Example 5.
[0108]   Fig. 37 is SEM photograph (3,500 magnifications) of the complex oxide obtained in Comparative Example 5.
[0109]   Fig. 38 is SEM photograph (10,000 magnifications) of the complex oxide obtained in Comparative Example 5.
[0110]   Fig. 39 is XRD of the complex oxide obtained in Comparative Example 15.
[0111]   Fig. 40 is SEM photograph (20,000 magnifications) of the complex oxide obtained in Comparative Example 15.

Best Modes for Carrying Out the Invention

[0112]   The present invention is more specifically illustrated by the following examples.
[0113]   The respective methods for measuring the BET specific surface area, for measuring primary particle size by Scherrer's method and for measuring trivalent nickel carryed out with restect to the heat - treated product are as shown below.

[A method for measuring BET specific surface area]

[0114]   A given amount of the heat-treated product was weighed in a cell as the sample to be employed and degassed by heating under the flow of a mixed gas of 30 % nitrogen and 70 % helium, and thereafter specific surface area was measured according to the BET one point continuous flowing method. As BET specific surface area measuring apparatus, "MONOSORB" a product of Yuasa Ionics Co., Ltd. was employed.

[Scherrer's method]

[0115] It is a method wherein the size of crystallite is calculated by the following equation (1) on the assumption that the width of diffraction pattern is dependent on the size of crystallite alone owing to uniformity in the size of crystallite and no strain in the crystals.

$$Dhkl = (k\lambda) / (\beta cos\theta) \qquad \text{(Equation 1)}$$

wherein Dhkl (angstrom) represents size of crystallite in vertical direction to the face (hkl), λ (angstrom) the wavelength of X-ray, β (rad) the width of diffraction pattern, θ (°) angle of diffraction, and k a constant.

[A method for measuring Ni^{3+}]

[0116] Ni^{3+} is expressed in percentage based on the total Ni. It was measured by oxidation-reduction titration. 0.2 gram of a sample was dissolved in 0.25 M $FeSO_4$- 3.6 N H_2SO_4 solution, and 2 ml of a concentrated phosphoric acid was added to the solution. The mixture was titrated with a 0.1 N $KMnO_4$ solution. Blank test was carried out in the same manner as in the above. The Ni^{3+} % was calculated by the following equation 2. In the equation 2, f represents the factor of the 0.1 N $KMnO_4$ solution, X_0 the titer of the blank test (ml), X the titer of the sample (ml), m the amount of the sample (g), and B the content of Ni (%) and A 5.871.

$$[fX (X_0\text{-}X) \times A \times 10] / (m \times B) \qquad \text{(Equation 2)}$$

Example 1

[0117] There was prepared a mixed aqueous solution of 2.0 mol/l aluminum nitrate and nickel nitrate wherein the molar ratio of Al / (Ni + Al) was 0.03. This mixed aqueous solution and 2.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 50°C for about 60 minutes with vigorous stirring while pH was kept to 9.0.
[0118] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.97}Al_{0.03}(OH)_2(NO_3)_{0.03}$ slurry. A 3.5 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Al) was 1.05 with respect to the (Ni + Al) content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.
[0119] The chemical composition of the firing product was $Li_{1.03}Ni_{0.97}Al_{0.03}O_2$.

Example 2

[0120] There was prepared a mixed aqueous solution of 2.0 mol/l aluminum nitrate and nickel nitrate wherein the molar ratio of Al / (Ni + Al) was 0.02. This mixed aqueous solution and 2.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 50°C over the period of about 60 minutes with vigorous stirring while pH was kept to 9.5.
[0121] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.98}Al_{0.02}(OH)_2(NO_3)_{0.02}$ slurry. A 3.5 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Al) was 1.03 with respect to the (Ni + Al) content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.
[0122] The chemical composition of the heat-treated product was $Li_{1.01}Ni_{0.98}Al_{0.02}U_2$.

Example 3

[0123] There was prepared a mixed aqueous solution of 2.0 mol/l aluminum nitrate and nickel nitrate wherein the molar ratio of Al / (Ni + Al) was 0.1. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C over the period of about 60 minutes with vigorous stirring while pH was kept to 8.5.
[0124] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.9}Al_{0.1}(OH)_2(NO_3)_{0.1}$ slurry. A 3.5 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Al) was 1.05 with respect to the (Ni + Al) content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was

put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0125] The chemical composition of the heat - treated product was $LiNi_{0.9}Al_{0.1}O_2$.

Example 4

[0126] There was prepared a mixed aqueous solution of 2.0 mol/l aluminum nitrate and nickel nitrate wherein the molar ratio of Al / (Ni + Al) was 0.2. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C over the period of about 60 minutes with vigorous stirring while pH was kept to 8.5.

[0127] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.8}Al_{0.2}(OH)_2(N0_3)_{0.2}$ slurry.A 3.5 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Al) was 1.05 with respect to the (Ni + Al) content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0128] The chemical composition of the heat - treated product was $Li_{1.01}Ni_{0.8}Al_{0.2}O_2$.

Example 5

[0129] The spray dried product obtained in Example 3 was pressed into a shape under a static pressure of 1,000 kg/ cm^2 using Brinell hardness tester. The shaped form was put in an alumina boat and fired at 750°C for 72 hours in an atmosphere of oxygen in a tube furnace. After cooling on standing, the heat-treated product was pulverized to obtain powdery $LiNi_{0.9}Al_{0.1}O_2$.

Example 6

[0130] There was prepared a mixed aqueous solution of 2.0 mol/l ferric nitrate and nickel nitrate wherein the molar ratio of Fe / (Ni + Fe) was 0.03. This mixed aqueous solution and 2.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 50 °C over the period of about 60 minutes with vigorous stirring while pH was kept to 9.5.

[0131] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.97}Fe_{0.03}(OH)_2(NO_3)_{0.03}$ slurry. A 3.5 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Fe) was 1.03 with respect to the (Ni + Fe) content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in a alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0132] The chemical composition of the heat-treated product was $Li_{1.02}Ni_{0.97}Fe_{0.03}O_2$.

Example 7

[0133] There was prepared a mixed aqueous solution of 2.0 mol/l ferric nitrate and nickel nitrate wherein the molar ratio of Fe / (Ni + Fe) was 0.1. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.

[0134] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.}Ni_{0.9}Fe_{0.1}(OH)_2(NO_3)_{0.1}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Fe) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in a alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0135] The chemical composition of the heat - treated product was $LiNi_{0.9}Fe_{0.1}O_2$.

Example 8

[0136] There was prepared a mixed aqueous solution of 2.0 mol/l ferric nitrate and nickel nitrate wherein the molar ratio of Fe / (Ni + Fe) was 0.2. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.

[0137] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.8}Fe_{0.2}(OH)_2(NO_3)_{0.2}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Fe) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in a alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0138] The chemical composition of the heat-treated product was $LiNi_{0.8}Fe_{0.2}O_2$.

Example 9

[0139] The spray dried product obtained in Example 7 was pressed into a shape under a static pressure of 1,000 kg/ cm^2 using Brinell hardness tester. The shaped form was put in an alumina boat and heated at 750 °C for 20 hours in an atmosphere of oxygen in a tube furnace. After cooling on standing, the heat-treated product was pulverized to obtain powdery $LiNi_{0.9}Fe_{0.1}O_2$.

Example 10

[0140] There was prepared a mixed aqueous solution of 1.0 mol/l manganese nitrate and nickel nitrate wherein the molar ratio of Mn / (Ni + Mn) was 0.03. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.
[0141] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.97}Mn_{0.03}(OH)_{1.97}(NO_3)_{0.03}$ slurry, (this basic nitrate salt was dried and the resultant dry one has a BET specific surface area of 147.18 m^2/g and a primary particle size (crystal lattice) of 44.1 angstroms as the value calculated by Scherrer's method from the half value width of the peak appeared at near 2θ = 60° of XRD). A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Mn) was 1.05 with respect to the Ni content in the above suspension to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace and pulverized in a mortarto obtain powdery $LiNi_{0.97}Mn_{0.03}O_2$.

Example 11

[0142] There was prepared a mixed aqueous solution of 1.0 mol/l manganese nitrate and nickel nitrate wherein the molar ratio of Mn / (Ni + Mn) was 0.1. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25 °C with vigorous stirring while pH was kept to 8.5.
[0143] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.9}Mn_{0.1}(OH)_{1.9}(NO_3)_{0.1}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Mn) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.
[0144] The chemical composition of the heat-treated product was $LiNi_{0.9}Mn_{0.1}O_2$.

Example 12

[0145] There was prepared a mixed aqueous solution of 1.0 mol/l manganese nitrate and nickel nitrate wherein the molar ratio of Mn / (Ni + Mn) was 0.4. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25 °C with vigorous stirring while pH was kept to 8.5.
[0146] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.6}Mn_{0.4}(OH)_{1.7}(NO_3)_{0.3}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Mn) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.
[0147] The chemical composition of the heat - treated product (powder) was $LiNi_{0.6}Mn_{0.4}O_2$.

Example 13

[0148] The spray dried product obtained in Example 11 was pressed into a shape under a static pressure of 1,000 kg/cm^2 using Brinell hardness tester. The shaped form was put in an alumina boat and heated at 750 °C for 20 hours in an atmosphere of oxygen in a tube furnace. After cooling on standing, the heat-treated product was pulverized to obtain powdery $LiNi_{0.9}Mn_{0.1}O_2$.

Example 14

[0149] There was prepared a mixed aqueous solution of 2.0 mol/l cobalt nitrate and nickel nitrate wherein the molar ratio of Co / (Ni + Co) was 0.03. This mixed aqueous solution and 2.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 40 °C over the period of about 60 minutes with vigorous stirring while pH was kept to 9.0.
[0150] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a

1 mol/l $Ni_{0.97}Co_{0.03}(OH)_2(NO_3)_{0.03}$ slurry. A 3.5 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Co) was 1.05 with respect to the (Ni + Co) content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0151] The chemical composition of the heat - treated product was $Li_{1.03}Ni_{0.97}Co_{0.03}O_2$.

Example 15

[0152] There was prepared a mixed aqueous solution of 1.0 mol/l cobalt nitrate and nickel nitrate wherein the molar ratio of Co / (Ni + Co) was 0.1. This mixed aqueous solution and 2.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.

[0153] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.9}Co_{0.1}(OH)_{1.9}NO_3)_{0.1}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Co) was 1.05 with respect to the Ni content in the above suspension to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace to obtain powdery $LiNi_{0.9}Co_{0.1}O_2$.

Example 16

[0154] There was prepared a mixed aqueous solution of 1.0 mol/l cobalt nitrate and nickel nitrate wherein the molar ratio of Co / (Ni + Co) was 0.2. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.

[0155] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.8}Co_{0.2}(OH)_{1.9}NO_3)_{0.2}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Co) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace to obtain powdery $LiNi_{0.8}Co_{0.2}O_2$.

Example 17

[0156] There was prepared a mixed aqueous solution of 1.0 mol/l cobalt nitrate and nickel nitrate wherein the molar ratio of Co / (Ni + Co) was 0.3. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.

[0157] The obtained precipitate was filtered out, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.7}Co_{0.3}(OH)_{1.7}(NO_3)_{0.3}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Co) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace to obtain powdery $LiNi_{0.7}Co_{0.3}O_2$.

Example 18

[0158] There was prepared a mixed aqueous solution of 1.0 mol/l cobalt nitrate and nickel nitrate wherein the molar ratio of Co / (Ni + Co) was 0.4. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.

[0159] The obtained precipitate was filtered out, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.6}Co_{0.4}(OH)_{1.7}(NO_3)_{0.3}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Co) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace to obtain powdery $LiNiO_{0.6}Co_{0.4}O_2$.

Example 19

[0160] There was prepared a mixed aqueous solution of 1.0 mol/l cobalt nitrate and nickel nitrate wherein the molar ratio of Co / (Ni + Co) was 0.2. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were

simultaneously added at 25°C with vigorous stirring while pH was kept to 11.5.

[0161]   The obtained precipitate was filtered out, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.8}C_{0.2}(OH)_{1.7}(NO_3)_{0.3}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Co) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained spray-dried product was pressed into a shape under a static pressure of 1,300kg/cm^2 Brinell hardness tester. The shaped form was put in an alumina boat and heated at 750 °C for 72 hours in an atmosphere of oxygen in a tube furnace. After cooling on standing, the heat-treated product was pulverized to obtain powdery $LiNi_{0.8}Co_{0.2}O_2$.

Example 20

[0162]   The spray dried product obtained in Example 15 was pressed into a shape under a static pressure of 1,000 kg/cm^2 using Brinell hardness tester. The shaped form was put in an alumina boat and heated at 750 °C for 20 hours in an atmosphere of oxygen in a tube furnace. After cooling on standing, the heat-treated product was pulverized to obtain powdery $LiNi_{0.9}Co_{0.1}O_2$.

Example 21

[0163]   There was prepared a mixed aqueous solution of 1.0 mol/l magnesium nitrate and nickel nitrate wherein the molar ratio of Mg / (Ni + Mg) was 0.049. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25 °C with vigorous stirring while pH was kept to 11.0.

[0164]   The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.951}Mg_{0.049}(OH)_{1.7}(NO_3)_{0.3}$ slurry. (The BET specific surface area of the dried basic nitrate salt was 169.4 m^2/g and its primary particle size (crystal lattice) was 32.3 angstroms as the value calculated by the Scherrer's method from the half value width of the peak appeared at near $2\theta = 60°$ of XRD). A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Mg) was 1.0 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The spray dried material was put in an alumina boat, heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace and pulverized in a mortar to obtain powdery $LiNi_{0.97}Mg_{0.05}O_2$.

Example 22

[0165]   The spray dried product obtained in Example 15 was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen. After cooling on standing, the firing product was pulverized and pressed into a shape under a static pressure of 1,300 kg/cm^2 using Brinell hardness tester. The press shaped form was once more put in an alumina boat and heated at 800 °C for 1 hour in an atmosphere of oxygen in a tube furnace. After cooling on standing, the heat-treated product was pulverized to obtain powdery $LiNi_{0.9}Co_{0.1}O_2$.

Comparative Example 1

[0166]   1,900 ml of 1.0 mol/l aqueous sodium hydroxide solution was added under stirring to 500 ml of 2.0 mol/l aqueous nickel nitrate solution, thus the molar ratio of Na/Ni being 1.9. The resultant reaction mixture was filtered, washed with water and suspended in water, thereby obtaining 1 mol/l $Ni(OH)_{1.97}(NO_3)_{0.03}$ slurry. A 3.5 mol/l aqueous lithium hydroxide solution was added dropwisely in an amount such that the atomic ratio of Li/Ni was 1.05 with respect to the Ni content in the slurry to effect a reaction. Thereafter, the reaction mixture was spray dried. The obtained dried gel was put in an alumina boat, and heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0167]   The chemical composition of the heat - treated product was $Li_{1.02}NiO_2$.

Comparative Example 2

[0168]   1.05 mol sodium hydroxide, 0.97 mol nickel hydroxide and 0.03 mol aluminum hydroxide were sufficiently mixed in dry state and pulverized in a mortar, and then pelletized into size of 14 mm of a diameter $\times$ 2 mm of a thickness. The resultant pellets were heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0169]   The chemical composition of the heat-treated product was $Li_{1.04}Ni_{0.97}Al_{0.03}O_2$.

Comparative Example 3

[0170]   1.05 mol sodium hydroxide, 0.97 mol nickel hydroxide and 0.03 mol ferric oxide were sufficiently mixed in dry

state and pulverized in a mortar, and then pelletized into size of 14 mm of a diameter $\times$ 2 mm of a thickness. The resultant pellets were heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0171] The chemical composition of the heat - treated product was $Li_{1.04}Ni_{0.97}Fe_{0.03}O_2$.

Comparative Example 4

[0172] 1.05 mol sodium hydroxide, 0.97 mol nickel hydroxide and 0.03 mol manganese dioxide were sufficiently mixed in dry state and pulverized in a mortar, and then pelletized into size of 14 mm of a diameter $\times$ 2 mm of a thickness. The resultant pellets were heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0173] The chemical composition of the heat-treated product was $Li_{1.04}Ni_{0.97}Mn_{0.03}O_2$.

Comparative Example 5

[0174] 1.05 mol sodium hydroxide, 0.97 mol nickel hydroxide and 0.03 mol cobalt hydroxide were sufficiently mixed in dry state and pulverized in a mortar, and then pelletized into size of 14 mm of a diameter $\times$ 2 mm of a thickness. The resultant pellets were heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0175] The chemical composition of the heat-treated product was $Li_{1.04}Ni_{0.97}Co_{0.03}O_2$.

Comparative Example 6

[0176] 1.05 mol sodium hydroxide, 0.97 mol nickel hydroxide and 0.03 mol magnesium oxide were sufficiently mixed in dry state and pulverized in a mortar, and then pelletized into size of 14 mm of a diameter $\times$ 2 mm of a thickness. The resultant pellets were heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0177] The chemical composition of the heat-treated product was $Li_{1.04}Ni_{0.97}Mg_{0.03}O_2$.

Comparative Example 7

[0178] There was prepared a mixed aqueous solution of 2.0 mol/l aluminum nitrate and nickel nitrate wherein the molar ratio of Al / (Ni + Al) was 0.3. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.

[0179] The obtained precipitate was filtered out, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.7}Al_{0.3}(OH)_2(NO_3)_{0.3}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Al) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0180] The chemical composition of the heat - treated product was $LiNi_{0.7}Al_{0.3}O_2$.

Comparative Example 8

[0181] There was prepared a mixed aqueous solution of 2.0 mol/l ferric nitrate and nickel nitrate wherein the molar ratio of Fe / (Ni + Fe) was 0.3. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.

[0182] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.7}Fe_{0.3}(OH)_2(NO_3)_{0.3}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Fe) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in a alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace.

[0183] The chemical composition of the heat-treated product was $LiNi_{0.7}Fe_{0.3}O_2$.

Comparative Example 9

[0184] There was prepared a mixed aqueous solution of 1.0 mol/l magnesium nitrate and nickel nitrate wherein the molar ratio of Mg / (Ni + Mg) was 0.3. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 11.0.

[0185] The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.7}Mg_{0.3}(OH)_{1.7}(NO_3)_{0.3}$. slurry A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Mg) was 1.0 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in

an alumina boat and heated at 750 °C for 5 hours in an atmosphere of oxygen in a tube furnace to obtain powdery $LiNi_{0.7}Mg_{0.3}O_2$.

Comparative Example 10

[0186]   There was prepared a mixed aqueous solution of 1.0 mol/l manganese nitrate and nickel nitrate wherein the molar ratio of Mn / (Ni + Mn) was 0.6. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.

[0187]   The obtained reaction mixture was filtered, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.4}Mn_{0.6}(OH)_{1.7}(NO_3)_{0.3}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Mn) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained dry material was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace to obtain powdery $LiNi_{0.4}Mn_{0.6}O_2$.

Comparative Example 11

[0188]   There was prepared a mixed aqueous solution of 1.0 mol/l cobalt nitrate and nickel nitrate wherein the molar ratio of Co / (Ni + Co) was 0.6. This mixed aqueous solution and 1.0 mol/l aqueous sodium hydroxide solution were simultaneously added at 25°C with vigorous stirring while pH was kept to 8.5.

[0189]   The obtained precipitate was filtered out, washed with water and suspended in water thereby obtaining a 1 mol/l $Ni_{0.4}Co_{0.6}(OH)_{1.7}(NO_3)_{0.3}$ slurry. A 3.0 mol/l aqueous lithium hydroxide solution was added dropwisely to the obtained slurry in an amount such that the atomic ratio of Li / (Ni + Co) was 1.05 with respect to the Ni content in the above slurry to effect reaction. Thereafter, the reaction mixture was spray dried. The obtained spray-dried product was put in an alumina boat and heated at 750°C for 5 hours in an atmosphere of oxygen in a tube furnace, and then pulverized in a mortar to obtain powdery $LiNi_{0.4}Co_{0.6}O_2$.

Comparative Example 12

[0190]   1.05 mol sodium hydroxide, 0.9 mol nickel hydroxide and 0.1 mol aluminum hydroxide were sufficiently mixed in dry state and pulverized in a mortar, and then pressed into a shape under a static pressure of 1,000kg/cm^2 using Brinell hardness tester. The shaped form was put in an alumina boat and heated at 750 °C for 20 hours in an atmosphere of oxygen in a tube furnace. After cooling on standing, the heat-treated product was pulverized to obtain powdery $LiNi_{0.9}Al_{0.1}O_2$.

Comparative Example 13

[0191]   1.05 mol sodium hydroxide, 0.9 mol nickel hydroxide and 0.1 mol ferric oxide were sufficiently mixed in dry state and pulverized in a mortar, and then pressed into a shape under a static pressure of 1,000kg/cm^2 using Brinell hardness tester. The shaped form was put in an alumina boat and heated at 750 °C for 20 hours in an atmosphere of oxygen in a tube furnace. After cooling on standing, the heat-treated product was pulverized to obtain powdery $LiNi_{0.9}Fe_{0.1}O_2$.

Comparative Example 14

[0192]   1.05 mol sodium hydroxide, 0.9 mol nickel hydroxide and 0.1 mol manganese dioxide were sufficiently mixed in dry state and pulverized in a mortar, and then pressed into a shape under a static pressure of 1,000 kg/cm^2 using Brinell hardness tester. The shaped form was put in an alumina boat and heated at 750 °C for 20 hours in an atmosphere of oxygen in a tube furnace. After cooling on standing, the heat-treated product was pulverized to obtain powdery $LiNi_{0.9}Mn_{0.1}O_2$.

Comparative Example 15

[0193]   1.05 mol sodium hydroxide, 0.9 mol nickel hydroxide and 0.1 mol cobalt hydroxide were sufficiently mixed in dry state and pulverized in a mortar, and then pressed into a shape under a static pressure of 1,000 kg/cm^2 using Brinell hardness tester. The shaped form was put in an alumina boat and heated at 750 °C for 20 hours in an atmosphere of oxygen in a tube furnace. After cooling on standing, the heat-treated product was pulverized to obtain powdered $LiNi_{0.9}Co_{0.1}O_2$.

[0194] Tables 1 and 2 show the ratios in X-ray peak intensity (003)/(104) and (006)/(101) calculated from the X-ray diffraction patterns , BET specific surface area, Ni^{3+} ratio (%), an average secondary particle size as measured by laser microtrack and long diameter of primary particle obtained from the SEM photograph, measured with respect to each of the compound oxides obtained in Examples 1 ~ 22 and Comparative Examples 1 ~ 15.

Table 1

The physical properties of the complex oxides obtained in Examples 1 ~ 22						
Example No.	Ni^{3+} (%)	BET m^2/g	Ratio of I(003)/I(104)	Ratio of I(006)/I(101)	Average Particle Size (μ)	Average Long Diameter of Primary Particle as Obserbed by SEM (μ)
1	99.4	0.44	1.43	0.119	15.91	0.51
2	99.7	0.51	1.48	0.114	19.61	0.40
3	99.6	0.30	1.49	0.113	18.21	0.40
4	99.3	0.32	1.53	0.111	16.41	0.35
5	99.8	0.09	1.57	0.118	-	5.0
6	99.1	0.31	1.4	0.112	16.57	0.45
7	99.6	0.12	1.5	0.110	15.41	0.29
8	99.7	0.28	1.5	0.120	16.22	0.31
9	99.9	0.06	1.5	0.122	-	6.30
10	99.7	0.41	1.324	0.119	6.04	0.45
11	99.3	0.58	1.4	0.121	21.09	0.39
12	99.3	0.43	1.5	0.117	18.67	0.41
13	99.8	0.08	1.5	0.121	-	4.0
14	99.8	0.42	1.4	0.110	15.51	0.37
15	99.4	0.58	1.5	0.115	18.96	0.43
16	99.8	0.36	1.65	0.121	20.60	0.45
17	99.6	0.61	1.4	0.120	16.40	0.45
18	99.8	0.82	1.4	0.119	16.83	0.41
19	99.9	0.07	1.323	0.113	-	3.8
20	99.8	0.10	1.4	0.118	-	4.0
21	99.8	0.17	1.304	0.115	58.66	0.45
22	99.9		1.4	0.118	-	3.4

Table 2

The physical properties of the complex oxides obtained in Comparative Examples 1 ~ 15						
Comparative Example No.	Ni^{3+} (%)	BET m^2/g	Ratio of I(003)/I(104)	Ratio of I(006)/I(101)	Average Particle Size (μ)	Average Long Diameter of Primary Particle as Obserbed by SEM (μ)
1	98.8	0.13	1.45	0.115	20.70	0.61
2	95.3	0.47	1.23	0.132	-	0.40
3	93.1	0.35	1.29	0.140	-	0.38
4	92.3	0.34	1.28	0.143	-	0.47
5	90.1	0.42	1.21	0.148	-	0.23

Table 2   (continued)

The physical properties of the complex oxides obtained in Comparative Examples 1 ~ 15						
Comparative Example No.	Ni^{3+} (%)	BET m^2/g	Ratio of I(003)/ I(104)	Ratio of I(006)/ I(101)	Average Particle Size (μ)	Average Long Diameter of Primary Particle as Obserbed by SEM (μ)
6	91.1	0.21	1.26	0.142	-	0.33
7	93.4	0.18	1.31	0.129	18.21	0.41
8	95.1	0.30	1.42	0.136	16.40	0.37
9	92.9	0.28	1.51	0.121	20.81	0.42
10	97.8	0.15	1.48	0.120	21.22	0.22
11	98.1	0.22	1.50	0.117	19.46	0.42
12	99.0	0.08	2.03	0.118	-	0.81
13	98.6	0.09	1.94	0.114	-	0.74
14	97.9	0.09	1.82	0.118	-	0.68
15	98.9	0.08	2.27	0.111	-	0.63
Also, the primary particle size of the basic metal salt (II) employed in the wet process of the present invention is shown in Table 3.						

Table 3

The physical properties of the basic metal salt employed in the reaction	
Example No.	Primary Particle Size/Scherrer's method (Angstrom)
Example 1	34.1
Example 2	41.4
Example 3	38.7
Example 4	36.3
Example 5	38.7
Example 6	42.9
Example 7	36.2
Example 8	42.9
Example 9	36.2
Example 10	44.1
Example 11	38.1
Example 12	37.2
Example 13	38.1
Example 14	43.4
Example 15	43.5
Example 16	31.2
Example 17	44.1
Example 18	40.4
Example 19	35.8
Example 20	43.5
Example 21	32.3
Example 22	38.8

The long diamter of the primary particle size for all of the spray dried and heat - treated complex oxides were in the range of 0.2 ~ 3.0μm.

Experiment 1

[0195] The following battery test (charge and discharge test) was carried out using the complex oxides obtained in Examples 1, 2, 6 and 14 and Comparative Examples 1, 2, 3 and 5.

[0196] For a positive electrode material, each of the lithium nickel complex oxides obtained in said Examples and said Comparative Examples was mixed with a conductive binder (polytetrafluoroethylene - acetylene black) in a weight ratio of 2:1. Thereafter, the mixture was formed into pellets each having a thickness of 0.5 mm and a diameter of 18 mm. The resultant pellets were press - bonded at a pressure of 1 t / cm^2 to an expanded stainless steel mesh by means of a pressing machine, thereby obtaining a positive electrode molding.

[0197] As a negative electrode material, a disk of 18 mm in diameter blanked from a lithium metal sheet was used. The positive electrode molding was put in a coin type cell composed of stainless steel, and an electrolyte in which 1 mol/l LiPF$_6$ was dissolved in a 1:4 mixture of propylene carbonate and ethylene carbonate was poured into the cell in an appropriate amount. A separator, the above negative electrode and its case were piled in this order on the electrolyte, thereby obtaining lithium secondary battery for test. All of the above procedures were conducted in an atmosphere of argon. The performance of the positive electrode active material was evaluated by repeating charging and discharging the thus obtained lithium secondary battery and measuring the initial discharge capacity and the discharge capacity decrease attributed to the repetition of charging and discharging. The above charging and discharging were performed under a voltage control between 3 V and 4.3 V at a constant current of 1 mA.

[0198] The results of the battery test [initial discharge capacity (mAh/g), discharge capacity at 100th cycle (mAh/g) and decrease rate of discharge capacity at 100th cycle (%)] are shown in Tables 4 and 5.

Table 4

Example No.	Initial Discharge Capacity (mAh/g)	Discharge Capacity at 100th Cycle (mAh/g)	Decrease Rate of Discharge Capacity at 100th Cycle (%)
1	157.0	145.5	7.3
2	161.0	146.6	8.9
6	160.1	148.2	7.4
14	160.2	146.2	8.7

Table 5

Comparative Example No.	Initial Discharge Capacity (mAh/g)	Discharge Capacity at 100th Cycle (mAh/g)	Decrease Rate of Discharge Capacity at 100th Cycle (%)
1	161.5	113.2	29.9
2	141.5	98.5	30.4
3	140.4	84.3	39.9
5	140.2	97.3	30.6

Experiment 2

[0199] The following battery test (charge and discharge test) was carried out using the complex oxides obtained in Examples 1 ~ 22 and Comparative Examples 1 ~ 15.

[0200] For a positive electrode material, each of the lithium nickel compound oxides obtained in the above Examples and Comparative Examples, etylene black as a conductive agent and polytetrafluoroethylene as a binder were mixed in a ratio of 88 6 : 6 % by weight. Thereafter, the mixture was subjected to compression molding on stainless steel mesh, thereby obtaining pellets each having a thickness of 5 mm and a diammeter of 18 mm. The resultant pellets were dried at 200°C for 2 hours, and used as a positive electrode material.

[0201] As a negative electrode material was used a rolled lithium metal sheet pressed - bonded to a stainless sub-strate. As a diaphragm, porous membrane made of polypropylene (trade name "Cell Guard", a product of Hoechst Japan Co., Ltd.) and a glass filter - paper filter were used. There was used an electrolyte in which 1 M LiClO$_4$ was dissolved in an ethylene carbonate/dimethylmethoxyeth ane mixture (1:1 weight ratio). The procedures up to comple-tion from setup of a test cell (semi - open type cell) were conducted in an argon replaced dry box. The charging and discharging for this lithium battery were performed under a voltage control between 3 V and 4.3 V at a constant current density of 0.4 mA/ cm^2.

[0202]   The results of the battery test [initial discharge capacity (mAh/g), discharge capacity at 100th cycle (mAh/g) and decrease rate of discharge capacity at 100th cycle (%)] are shown in Tables 6 and 7.

Table 6

Example No.	Initial Discharge Capacity (mAh/g)	Discharge Capacity at 100th Cycle (mAh/g)	Decrease Rate of Discharge Capacity at 100th Cycle (%)
1	187.9	174.9	6.9
2	181.2	166.2	8.3
3	169.1	161.8	4.3
4	151.0	139.8	7.5
5	158.0	154.0	3.5
6	167.6	153.7	8.3
7	144.8	132.5	8.5
8	142.3	131.3	7.7
9	136.1	129.7	4.7
10	166.4	156.7	5.8
11	168.7	159.3	5.6
12	154.3	141.8	8.1
13	157.8	150.8	4.4
14	171.2	157.3	8.1
15	171.1	164.2	7.3
16	182.9	168.1	8.1
17	171.3	165.8	3.2
18	163.0	153.5	5.8
19	172.4	165.8	3.8
20	159.8	152.1	4.8
21	162.6	151.9	6.6
22	161.3	154.8	4.0

Table 7

Comparative Example No.	Initial Discharge Capacity (mAh/g)	Discharge Capacity at 100th Cycle (mAh/g)	Decrease Rate of Discharge Capacity at 100th Cycle (%)
1	188.4	137.9	26.8
2	162.5	111.3	31.5
3	151.0	85.8	43.2
4	158.4	101.9	35.7
5	165.0	124.9	24.3
6	146.3	97.6	33.3
7	138.9	123.9	10.8
8	135.0	116.2	13.9
9	141.3	125.1	11.5
10	137.3	120.6	12.2
11	156.2	138.0	11.7
12	148.3	90.2	39.2
13	135.0	87.6	35.1
14	149.1	92.1	38.2
15	159.2	130.6	18.0

Experiment 3

[0203]   As an index indicating that the complex oxides obtained by the process of the present invention are stable at an elevated temperature, an exothermic reaction temperature of the positive electrode material after charging was measured by the following method.

[0204]   Using the test cell prepared in Experiment 2, the positive electrode material after charging was subjected to thermal analysis by DSC ("THERMOFLEX TAS200", a product of Rigaku Co., Ltd.) under an inert gas to maesure the exothermic reaction temperature.

[0205]   As a result, the peak of exothermic heat was recognized to appear at 208.6°C for Comparative Example 1, 224.3°C for Example 15 and at 237.6°C for Example 20.

[0206]   The temperature rise in the exothermic peak by introduction of Co etc. into $LiNiO_2$ was recognized. Furthermore, it is understood that the positive electrode material composed of larger primary particle size even among those having the same composition gives higher the exothermic peak temperature, thereby the stability of the positive electrode material at an elevated temperature is enhanced.

Industrial Applicability

[0207]   As explained above, according to the present invention there can be provided a novel process for preparing a lithium nickel complex oxide as claimed.

[0208]   The crystals obtained by said process are sufficiently developed and are highly purified, and a positive electrode active material for a secondary battery whose stability of high discharge capacity is excellent.

Claims

1.   A process for preparing a lithium nickel complex oxide represented by the general formula (I)

$$Li_{y-x1}Ni_{1-x2}M_xO_2 \qquad (I)$$

wherein M represents a metal selected from the group consisting of Al, Fe, Co, Mn and Mg, $x = x_1 + x_2$ and

(i) when M is Al or Fe, then x, x_1 and x_2 represent respectively $0 < x \leq 0.2$, $x_1 = 0$, and $x_2 = x$;
(ii) when M is Co or Mn, then x, x_1 and x_2 represent respectively $0 < x \leq 0.5$, $x_1 = 0$, and $x_2 = x$;
(iii) when M is Mg, then x, x_1 and x_2 represent respectively $0 < x < 0.2$, $0 < x_1 \leq 0.2$ and $0 < x_2 \leq 0.2$; and y represents $0.9 \leq y \leq 1.3$,

said process comprising the steps of :

(a) reacting a basic metal salt represented by the general formula (II)

$$Ni_{1-x}M^p{}_x(OH)_{2-nz}(A^{n-})_{[z+(px-2x)/n]} \cdot mH_2O \qquad (II)$$

wherein M represents a metal selected from the group consisting of Al, Fe, Co, Mn and Mg, p is a valence number of M with $2 \leq p \leq 3$, A^{n-} is an anion having a valence of n, and x, z and m are positive numbers respectively satisfying the ranges of $0 < x \leq 0.2$, $0.03 \leq z \leq 0.3$, $0 \leq m < 2$; with a water soluble lithium compound in an aqueous medium in a molar ratio of Li/(Ni+M) of $0.9 \sim 1.3$ to obtain a slurry,
(b) spray drying the obtained slurry; and
(c) heating the resultant dry material at a temperature of about 600°C $\sim$ 900°C for about 4 hours or more in an oxidative atmosphere.

2.   A process for preparing a lithium nickel complex oxide represented by the general formula (I)

$$Li_{y-x1}Ni_{1-x2}M_xO_2 \qquad (I)$$

wherein M represents a metal selected from the group consisting of Al, Fe, Co, Mn and Mg, $x = x_1 + x_2$, and

(i) when M is Al or Fe, then x, x_1 and x_2 -represent respectively $0 < x \leq 0.2$, $x_1 = 0$, and $x_2 = x$;
(ii) when M is Co or Mn, then x, x_1 and x_2 represent respectively $0 < x \leq 0.5$, $x_1 = 0$, and $x_2 = x$;
(iii) when M is Mg, then x, x_1 and x_2 represent respectively $0 < x \leq 0.2$, $0 < x_1 \leq 0.2$ and $0 < x_2 \leq 0.2$; and y represents $0.9 \leq y \leq 1.3$,

said process comprising the steps of:

(a) reacting a basic metal salt represented by the general formula (II)

$$Ni_{1-x}M^p{}_x(OH)_{2-nz}(A^{n-})_{[Z+(px-2x)/n]} \cdot mH_2O \tag{II}$$

wherein M represents a metal selected from the group consisting of Al, Fe, Co, Mn and Mg, p is a valence number of M with $2 \leq p \leq 3$, A^{n-} is an anion having a valence of n, and x, z and m are positive numbers respectively satisfying the ranges of $0 < x \leq 0.2$, $0.03 \leq z \leq 0.3$, $0 \leq m < 2$; with a water soluble lithium compound in an aqueous medium in a molar ratio of Li/(Ni+M) of $0.9 \sim 1.3$ to obtain a slurry,
(b) spray drying the obtained slurry;
(c) subjecting the spray dried product to press molding; and
(d) heating the molded product at a temperature of about $600°C \sim 900°C$ for about 4 hours or more in an oxidative atmosphere.

3. A process for preparing a lithium nickel complex oxide represented by the general formula (I)

$$Li_{y-x1}Ni_{1-x2}M_xO_2 \tag{I}$$

wherein M represents a metal selected from the group consisting of Al, Fe, Co, Mn and Mg, $x = x_1 + x_2$, and

(i) when M is Al or Fe, then x, x_1 and x_2 represent respectively $0 < x \leq 0.2$, $x_1 = 0$, and $x_2 = x$;
(ii) when M is Co or Mn, then x, x_1 and x_2 represent respectively $0 < x < 0.5$, $x_1 = 0$, and $x_2 = x$;
(iii) when M is Mg, then x, x_1 and x_2 represent respectively $0 < x \leq 0.2$, $0 < x_1 \leq 0.2$, and $0 < x_2 \leq 0.2$; and y represents $0.9 \leq y \leq 1.3$,

said process comprising the steps of:

(a) reacting a basic metal salt represented by the general formula (II)

$$Ni_{1-x}M^p{}_x(OH)_{2-nz}(A^{n-})_{[Z+(px-2x)/n]} \cdot mH_2O \tag{II}$$

wherein M represents a metal selected from the group consisting of Al, Fe, Co, Mn and Mg, p is a valence number of M with $2 \leq p \leq 3$, A^{n-} is an anion having a valence of n, and x, z and m are positive numbers respectively satisfying the ranges of $0 < x \leq 0.2$, $0.03 \leq z \leq 0.3$, $0 \leq m < 2$; with a water soluble lithium compound in an aqueous medium in a molar ratio of Li/(Ni+M) of $0.9 \sim 1.3$ to obtain a slurry,
(b) spray drying the obtained slurry;
(c) heating the spray dried product at a temperature of about $600°C \sim 900°C$ for about 0.5 hour or more in an oxidative atmosphere;
(d) pulverizing the resultant heat-treated product;
(e) subjecting the pulverized heat-treated product to press molding; and
(f) re-heating the molded product at a temperature of about $600°C \sim 900°C$ for about 1 hour or more in an oxidative atmosphere.

4. The process of claim 1 wherein M of the general formulae (I) and (II) is Al or Mg.

5. The process of claim 2 wherein M of the general formulae (I) and (II) is Al or Mg.

6. The process of claim 3 wherein M of the general formulae (I) and (II) is Al or Mg.

7. A positive electrode active material for a secondary battery which contains as an active ingredient the lithium nickel complex oxide prepared by the process as claimed in any one of claims 1 to 6.

8. The positive electrode active material for a secondary battery as claimed in claim 7 which the decrease rate of discharge capacity at 100th cycle based on the initial discharge capacity is 10% or less.

Patentansprüche

1. Verfahren zur Herstellung eines Lithium-Nickel-Komplexoxids, dargestellt durch die allgemeine Formel (I)

$$Li_{y-x1}Ni_{1-x2}M_xO_2 \quad\quad (I)$$

worin M ein Metall, ausgewählt aus der Gruppe bestehend aus Al, Fe, Co, Mn und M, bedeutet, $x = x_1 + x_2$, und

(i) wenn M Al oder Fe bedeutet, dann bedeuten x, x_1 bzw. x_2 $0 < x \leq 0,2$, $x_1 = 0$ und $x_2 = x$;
(ii) wenn M Co oder Mn bedeutet, dann bedeuten x, x_1 bzw. x_2 $0 < x \leq 0,5$, $x_1 = 0$ und $x_2 = x$;
(iii) wenn M Mg bedeutet, dann bedeuten x, x_1 bzw. x_2 $0 < x < 0,2$, $0 < x_1 \leq 0,2$ und $0 < x_2 \leq 0,2$; und y bedeutet $0,9 \leq y \leq 1,3$,

wobei das Verfahren die Stufen umfasst:

(a) Umsetzung eines basischen Metallsalzes, dargestellt durch die allgemeine Formel (II)

$$Ni_{1-x}M^p_x(OH)_{2-nz}(A^{n-})_{[Z+(px-2x)/n]} \cdot mH_2O \quad\quad (II)$$

worin M ein Metall bedeutet, ausgewählt aus der Gruppe bestehend aus Al, Fe, Co, Mn und Mg, p die Wertigkeitszahl von M mit $2 \leq p \leq 3$, A^{n-} ein Anion mit einer Wertigkeit von n bedeutet und x, z bzw. m positive Zahlen bedeuten, die die Bereiche $0 < x \leq 0,2$, $0,03 \leq z \leq 0,3$, $0 \leq m < 2$ umfassen; mit einer wasserlöslichen Lithiumverbindung in wässrigem Medium in einem Molverhältnis von Li/(Ni+M) von 0,9 ~ 1,3 unter Bildung einer Aufschlämmung,
(b) Sprühtrocknung der erhaltenen Aufschlämmung; und
(c) Erhitzen des entstehenden trockenen Materials bei einer Temperatur von etwa 600°C ~ 900°C während etwa 4 Stunden oder länger in oxidativer Atmosphäre.

2. Verfahren zur Herstellung eines Lithium-Nickel-Komplexoxids, dargestellt durch die allgemeine Formel (I)

$$Li_{y-x1}Ni_{1-x2}M_xO_2 \quad\quad (I)$$

worin M ein Metall, ausgewählt aus der Gruppe bestehend aus Al, Fe, Co, Mn und Mg, bedeutet, $x = x_1 + x_2$, und

(i) wenn M Al oder Fe bedeutet, dann bedeuten x, x_1 bzw. x_2 $0 < x \leq 0,2$, $x_1 = 0$ und $x_2 = x$;
(ii) wenn M Co oder Mn bedeutet, dann bedeuten x, x_1 bzw. x_2 $0 < x \leq 0,5$, $x_1 = 0$ und $x_2 = x$;
(iii) wenn M Mg bedeutet, dann bedeuten x, x_1 bzw. x_2 $0 < x \leq 0,2$, $0 < x_1 \leq 0,2$ und $0 < x_2 \leq 0,2$; und y bedeutet $0,9 \leq y \leq 1,3$,

wobei das Verfahren die Stufen umfasst:

(a) Umsetzung eines basischen Metallsalzes, dargestellt durch die allgemeine Formel (II)

$$Ni_{1-x}M^p_x(OH)_{2-nz}(A^{n-})_{[Z+(px-2x)/n]} \cdot mH_2O \quad\quad (II)$$

worin M ein Metall bedeutet, ausgewählt aus der Gruppe bestehend aus Al, Fe, Co, Mn und Mg, p die Wertigkeitszahl von M mit $2 \leq p \leq 3$, A^{n-} ein Anion mit einer Wertigkeit von n bedeutet und x, z bzw. m positive Zahlen bedeuten, die die Bereiche $0 < x \leq 0,2$, $0,03 \leq z \leq 0,3$, $0 \leq m < 2$ umfassen; mit einer wasserlöslichen Lithiumverbindung in wässrigem Medium in einem Molverhältnis von Li/(Ni+M) von $0,9 \sim 1,3$ unter Bildung einer Aufschlämmung,

(b) Sprühtrocknung der erhaltenen Aufschlämmung;

(c) Pressverformung des sprühgetrockneten Produkts; und

(d) Erhitzen des geformten Produkts bei einer Temperatur bei etwa $600°C \sim 900°C$ während etwa 4 Stunden oder länger in oxidativer Atmosphäre.

3. Verfahren zur Herstellung eines Lithium-Nickel-Komplexoxids, dargestellt durch die allgemeine Formel (I)

$$Li_{y-x1}Ni_{1-x2}M_xO_2 \tag{I}$$

worin M ein Metall, ausgewählt aus der Gruppe bestehend aus Al, Fe, Co, Mn und Mg, bedeutet, $x = x_1 + x_2$, und

(i) wenn M Al oder Fe bedeutet, dann bedeuten x, x_1 bzw. x_2 $0 < x \leq 0,2$, $x_1 = 0$ und $x_2 = x$;

(ii) wenn M Co oder Mn bedeutet, dann bedeuten x, x_1 bzw. x_2 $0 < x \leq 0,5$, $x_1 = 0$ und $x_2 = x$;

(iii) wenn M Mg bedeutet, dann bedeuten x, x_1 bzw. x_2 $0 < x \leq 0,2$, $0 < x_1 \leq 0,2$ und $0 < x_2 \leq 0,2$; und y bedeutet $0,9 \leq y \leq 1,3$,

wobei das Verfahren die Stufen umfasst:

(a) Umsetzung eines basischen Metallsalzes, dargestellt durch die allgemeine Formel (II)

$$Ni_{1-x}M^p{}_x(OH)_{2-nz}(A^{n-})_{[Z+px-2x)/n]} \cdot mH_2O \tag{II}$$

worin M ein Metall bedeutet, ausgewählt aus der Gruppe bestehend aus Al, Fe, Co, Mn und Mg, p die Wertigkeitszahl von M mit $2 \leq p \leq 3$, A^{n-} ein Anion mit einer Wertigkeit von n bedeutet und x, z bzw. m positive Zahlen bedeuten, die die Bereiche $0 < x \leq 0,2$, $0,03 \leq z \leq 0,3$, $0 \leq m < 2$ umfassen; mit einer wasserlöslichen Lithiumverbindung in wässrigem Medium in einem Molverhältnis von Li/(Ni+M) von $0,9 \sim 1,3$ unter Bildung einer Aufschlämmung,

(b) Sprühtrocknung der erhaltenen Aufschlämmung;

(c) Erhitzen des sprühgetrockneten Produkts bei einer Temperatur von etwa $600 \sim 900°C$ während etwa 0,5 Stunden oder länger in oxidativer Atmosphäre;

(d) Pulverisierung des entstehenden wärmebehandelten Produkts;

(e) Pressverformen des pulverisierten wärmebehandelten Produkts; und

(f) erneutes Erhitzen des geformten Produkts bei einer Temperatur von etwa $600°C \sim 900°C$ während etwa 1 Stunde oder länger in oxidativer Atmosphäre.

4. Verfahren nach Anspruch 1, wobei M in den allgemeinen Formeln (I) und (II) Al oder Mg bedeutet.

5. Verfahren nach Anspruch 2, wobei M in den allgemeinen Formeln (I) und (II) Al oder Mg bedeutet.

6. Verfahren nach Anspruch 3, wobei M in den allgemeinen Formeln (I) und (II) Al oder Mg bedeutet.

7. Aktives Material für eine positive Elektrode für eine Sekundärbatterie, das als aktiven Bestandteil das Lithium-Nickel-Komplexoxid, hergestellt gemäß dem Verfahren wie in einem der Ansprüche 1 bis 6 beansprucht, enthält.

8. Aktives Material für eine positive Elektrode für eine Sekundärbatterie nach Anspruch 7, wobei die Abnahmerate der Entladungskapazität beim 100. Zyklus, bezogen auf die Anfangsentladungskapazität, 10% oder weniger beträgt.

Revendications

1. Procédé de préparation d'un oxyde complexe de lithium-nickel représenté par la formule générale (I)

$$Li_{y-x1}Ni_{1-x2}M_xO_2 \qquad (I)$$

dans laquelle M représente un métal choisi dans le groupe constitué de Al, Fe, Co, Mn et Mg, x = x1 + x2 et

(i) quand M est Al ou Fe, alors x, x_1 et x_2 représentent respectivement $0 < x \leq 0,2$, $x_1 = 0$, et $x_2 = x$;
(ii) quand M est Co ou Mn, alors x, x_1 et x_2 représentent respectivement $0 < x \leq 0,5$, $x_1 = 0$, et $x_2 = x$;
(iii) quand M est Mg, alors x, x_1 et x_2 représentent respectivement $0 < x \leq 0,2$, $0 < x_1 \leq 0,2$ et $0 < x_2 \leq 0,2$; et

y représente $0,9 < y \leq 1,3$,
ledit procédé comprenant les étapes consistant à :

(a) faire réagir un sel de métal basique représenté par la formule générale (II)

$$Ni_{1-x}M^p{}_x(OH)_{2-nz}(A^{n-})_{[z+(px-2x)/n]} \cdot mH_2O \qquad (II)$$

dans laquelle M représente un métal choisi dans le groupe constitué de Al, Fe, Co, Mn et Mg, p est un nombre de valence de M avec $2 \leq p \leq 3$, A^{n-} est un anion ayant une valence de n, et x, z et m sont des nombres positifs compris respectivement dans les intervalles $0 < x \leq 0,2$, $0,03 \leq z \leq 0,3$, $0 \leq m < 2$; avec un composé de lithium soluble dans l'eau dans un milieu aqueux dans un rapport molaire Li/(Ni+M) de 0,9 à 1,3 pour obtenir une suspension épaisse,
(b) sécher par pulvérisation la suspension épaisse obtenue ; et
(c) chauffer le matériau sec obtenu à une température d'environ 600°C à 900°C pendant environ 4 heures ou plus dans une atmosphère oxydante.

2. Procédé de préparation d'un oxyde complexe de lithium-nickel représenté par la formule générale (I)

$$Li_{y-x1}Ni_{1-x2}M_xO_2 \qquad (I)$$

dans laquelle M représente un métal choisi dans le groupe constitué de Al, Fe, Co, Mn et Mg, x = x1 + x2 et

(i) quand M est Al ou Fe, alors x, x_1 et x_2 représentent respectivement $0 < x \leq 0,2$, $x_1 = 0$, et $x_2 = x$;
(ii) quand M est Co ou Mn, alors x, x_1 et x_2 représentent respectivement $0 < x \leq 0,5$, $x_1 = 0$, et $x_2 = x$;
(iii) quand M est Mg, alors x, x_1 et x_2 représentent respectivement $0 < x \leq 0,2$, $0 < x_1 \leq 0,2$ et $0 < x_2 \leq 0,2$; et

y représente $0,9 < y \leq 1,3$,
ledit procédé comprenant les étapes consistant à :

(a) faire réagir un sel de métal basique représenté par la formule générale (II)

$$Ni_{1-x}M^p{}_x(OH)_{2-nz}(A^{n-})_{[z+(px-2x)/n]} \cdot mH_2O \qquad (II)$$

dans laquelle M représente un métal choisi dans le groupe constitué de Al, Fe, Co, Mn et Mg, p est un nombre de valence de M avec $2 \leq p \leq 3$, A^{n-} est un anion ayant une valence de n, et x, z et m sont des nombres positifs compris respectivement dans les intervalles $0 < x \leq 0,2$, $0,03 \leq z \leq 0,3$, $0 \leq m < 2$; avec un composé de lithium soluble dans l'eau dans un milieu aqueux dans un rapport molaire Li/(Ni+M) de 0,9 à 1,3 pour obtenir une suspension épaisse,
(b) sécher par pulvérisation la suspension épaisse obtenue ;
(c) soumettre le produit séché par pulvérisation à un moulage par compression ; et
(c) chauffer le matériau sec obtenu à une température d'environ 600°C à 900°C pendant environ 4 heures ou

plus dans une atmosphère oxydante.

3. Procédé de préparation d'un oxyde complexe de lithium-nickel représenté par la formule générale (I)

$$Li_{y-x1}Ni_{1-x2}M_xO_2 \qquad (I)$$

dans laquelle M représente un métal choisi dans le groupe constitué de Al, Fe, Co, Mn et Mg, x = x1 + x2 et

(i) quand M est Al ou Fe, alors x, x_1 et x_2 représentent respectivement $0 < x \leq 0,2$, $x_1 = 0$, et $x_2 = x$;
(ii) quand M est Co ou Mn, alors x, x_1 et x_2 représentent respectivement $0 < x \leq 0,5$, $x_1 = 0$, et $x_2 = x$;
(iii) quand M est Mg, alors x, x_1 et x_2 représentent respectivement $0 < x \leq 0,2$, $0 < x_1 \leq 0,2$ et $0 < x_2 \leq 0,2$; et

y représente $0,9 < y \leq 1,3$,
ledit procédé comprenant les étapes consistant à :

(a) faire réagir un sel de métal basique représenté par la formule générale (II)

$$Ni_{1-x}M^p{}_x(OH)_{2-nz}(A^{n-})_{[z+(px-2x)/n]} \cdot mH_2O \qquad (II)$$

dans laquelle M représente un métal choisi dans le groupe constitué de Al, Fe, Co, Mn et Mg, p est un nombre de valence de M avec $2 \leq p \leq 3$, A^{n-} est un anion ayant une valence de n, et x, z et m sont des nombres positifs compris respectivement dans les intervalles $0 < x \leq 0,2$, $0,03 \leq z \leq 0,3$, $0 \leq m < 2$; avec un composé de lithium soluble dans l'eau dans un milieu aqueux dans un rapport molaire Li/(Ni+M) de 0,9 à 1,3 pour obtenir une suspension épaisse,
(b) sécher par pulvérisation la suspension épaisse obtenue ;
(c) chauffer le matériau sec obtenu à une température d'environ 600°C à 900°C pendant environ 0,5 heure ou plus dans une atmosphère oxydante ;
(d) pulvériser le produit traité par la chaleur résultant ;
(e) soumettre le produit pulvérisé traité par la chaleur à un moulage par compression ; et
(f) chauffer de nouveau le produit moulé à une température d'environ 600°C à 900°C pendant environ 1 heure ou plus dans une atmosphère oxydante.

4. Procédé selon la revendication 1, dans lequel M dans les formules générales (I) et (II) est Al ou Mg.

5. Procédé selon la revendication 2, dans lequel M dans les formules générales (I) et (II) est Al ou Mg.

6. Procédé selon la revendication 3, dans lequel M dans les formules générales (I) et (II) est Al ou Mg.

7. Matériau actif d'électrode positive pour une batterie d'accumulateurs qui contient comme substance active l'oxyde complexe de lithium-nickel préparé suivant le procédé selon l'une quelconque des revendications 1 à 6.

8. Matériau actif d'électrode positive pour une batterie d'accumulateurs selon la revendication 7, dont le taux de diminution de l'intensité de courant de décharge au 100ème cycle par rapport à l'intensité de courant de décharge initiale est de 10 % ou moins.

Fig. 1

XRD of the complex oxide obtained in Example 1
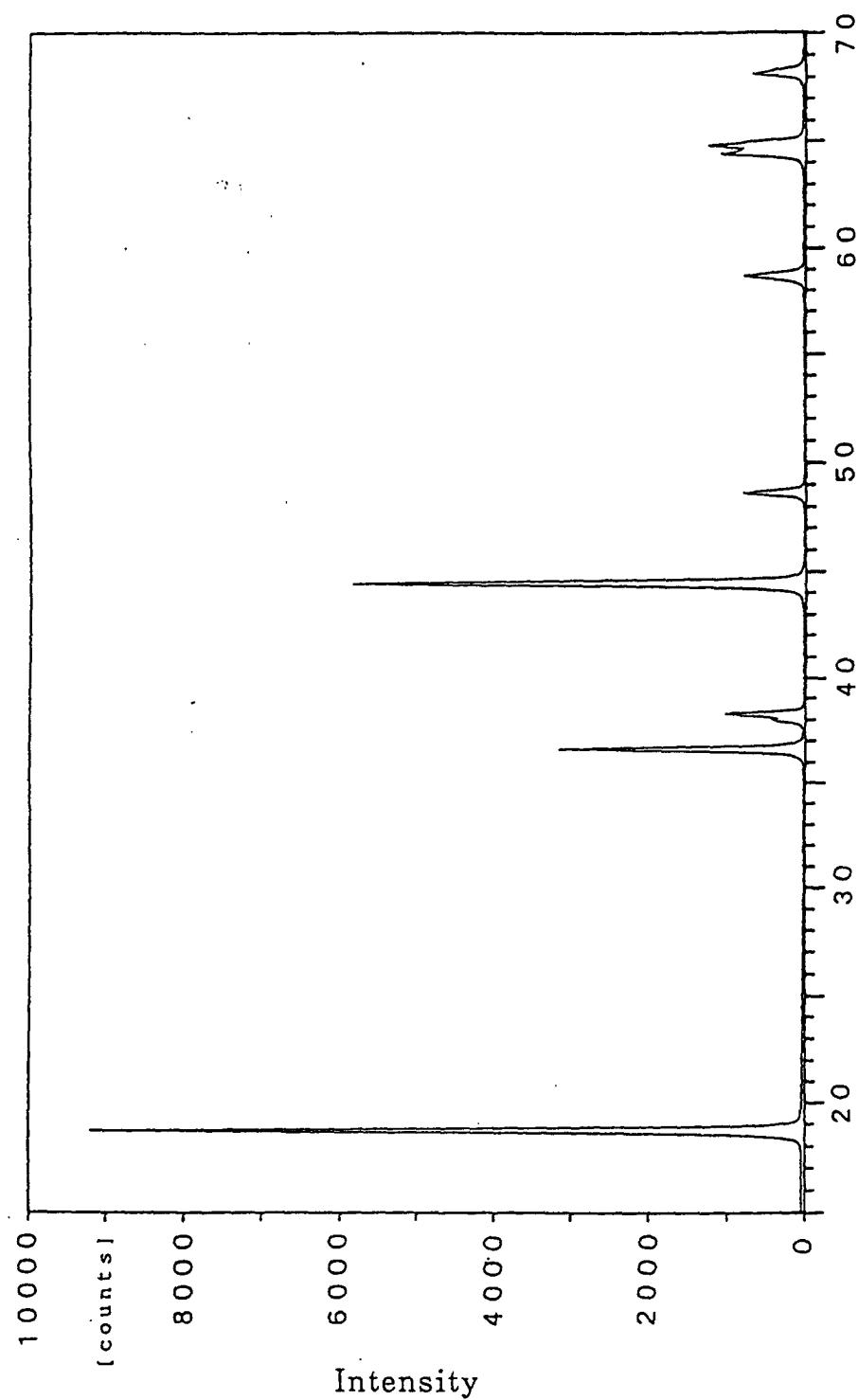
Fig. 2

SEM photograph (150 magnications) of the complex oxide obtained in Example 1
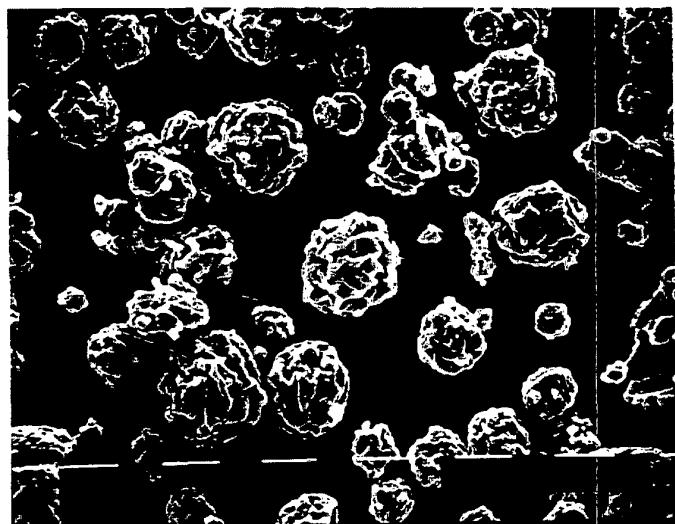
Fig. 3

SEM photograph (30,000 magnications) of the complex oxide obtained in Example 1
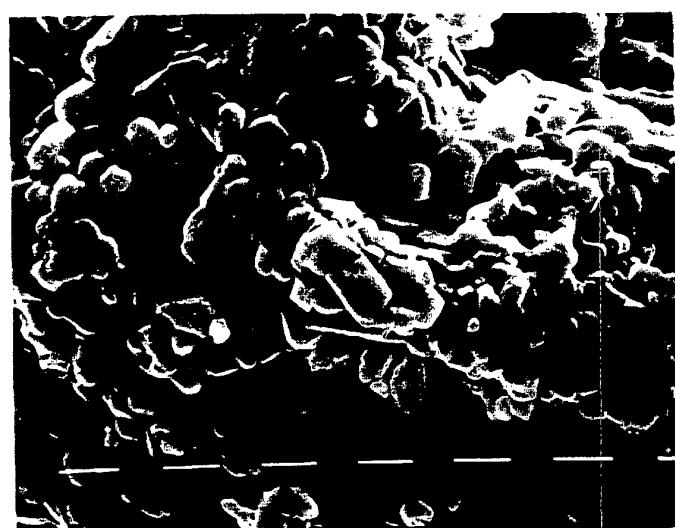
Fig. 4

Particle size distribution of the complex oxide
obtained in Example 1
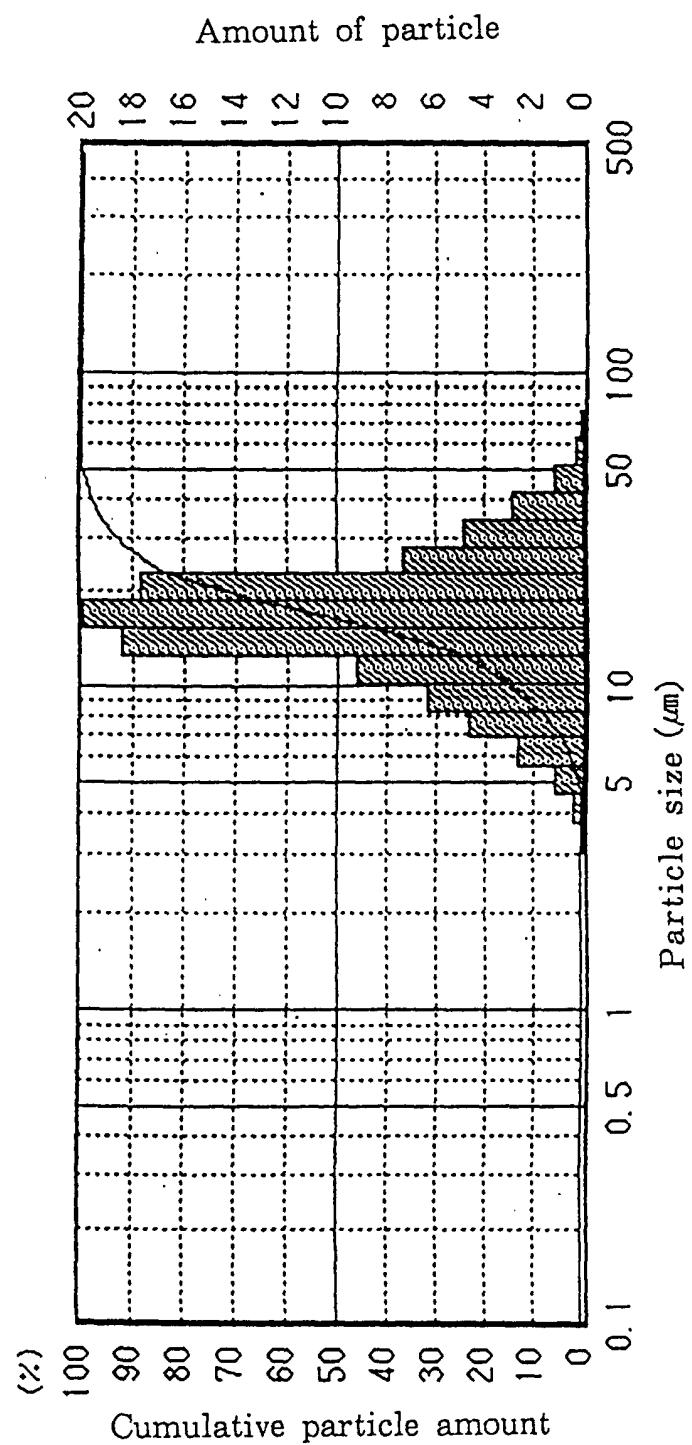
Fig. 5

XRD of the complex oxide obtained in Example 5
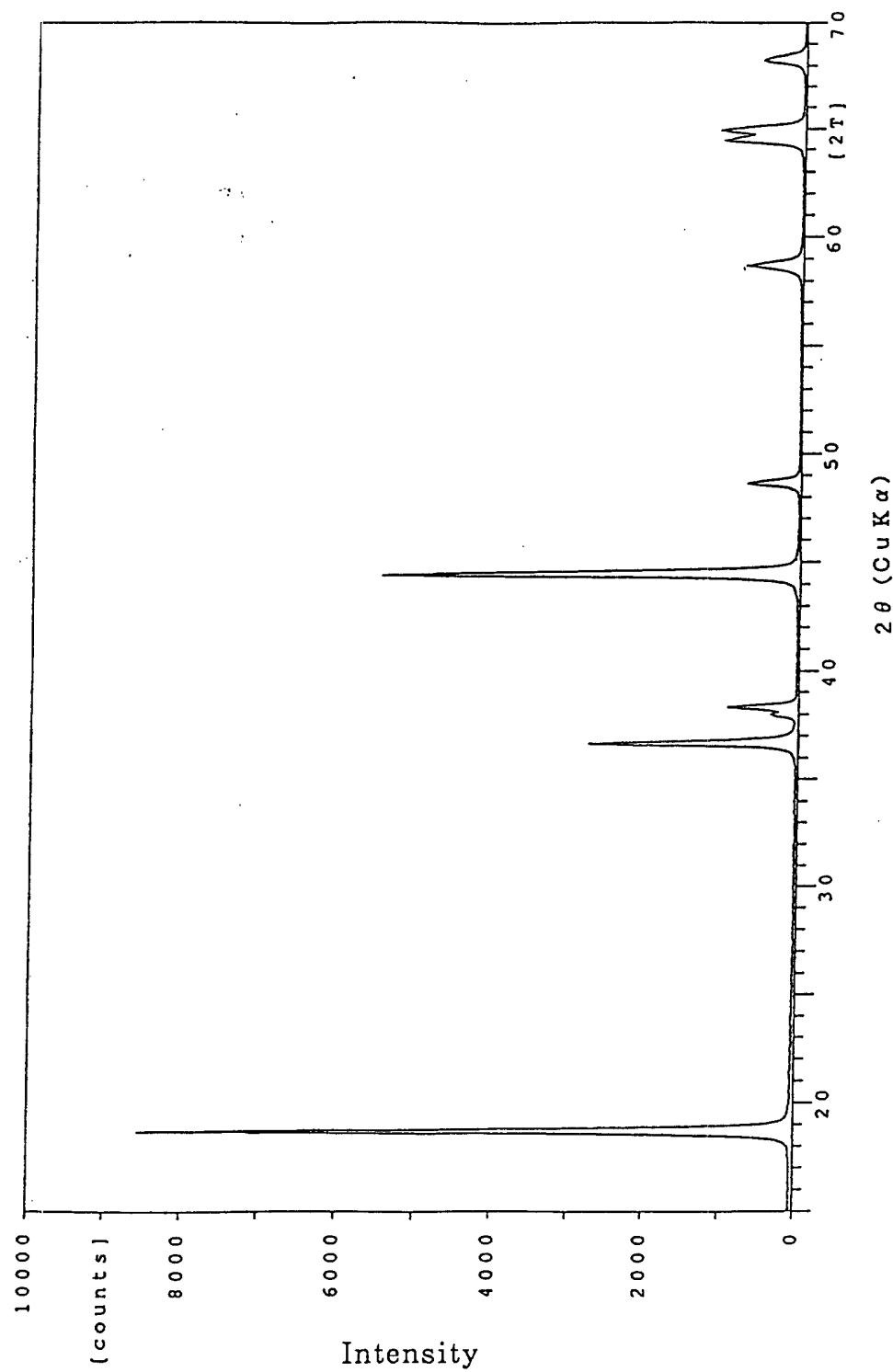
Fig. 6

SEM photograph (10,000 magnications) of the complex oxide obtained in Example 5
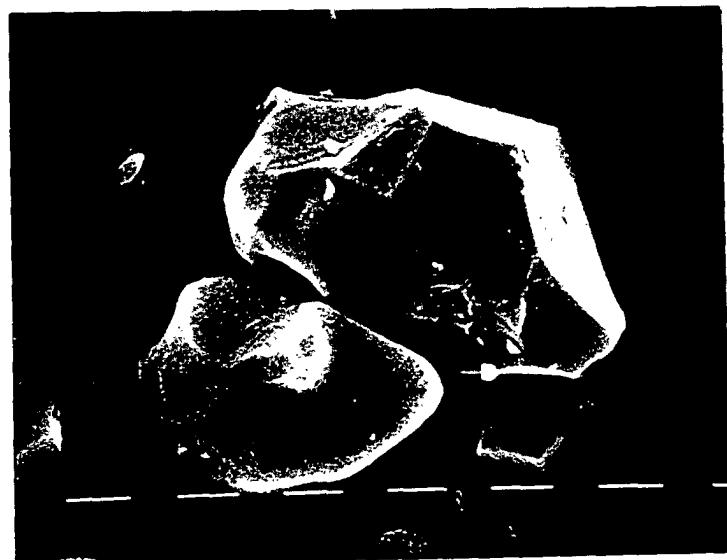
Fig. 7

XRD of the complex oxide obtained in Example 6
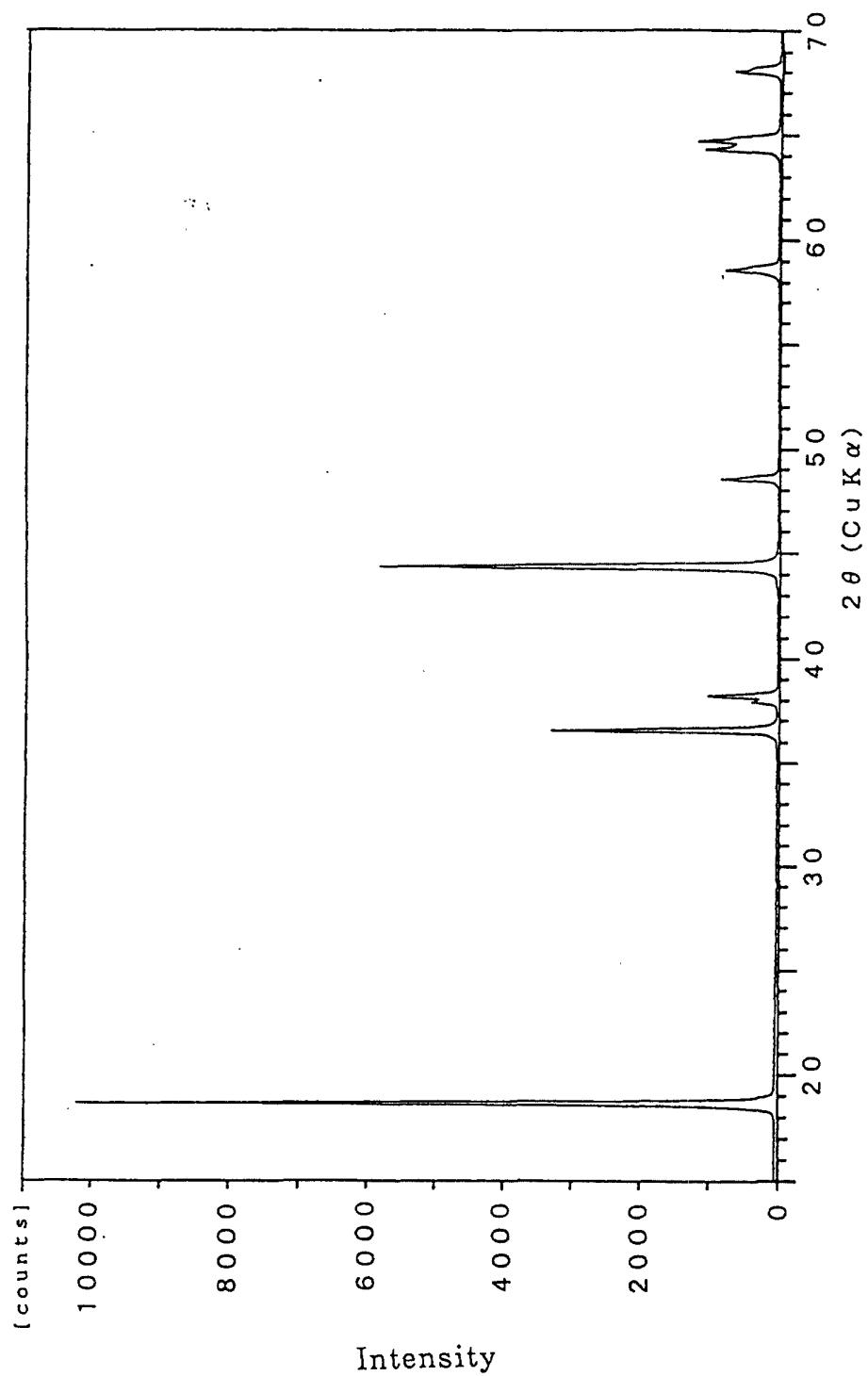
Fig. 8

SEM photograph (150 magnications) of the complex oxide
obtained in Example 6
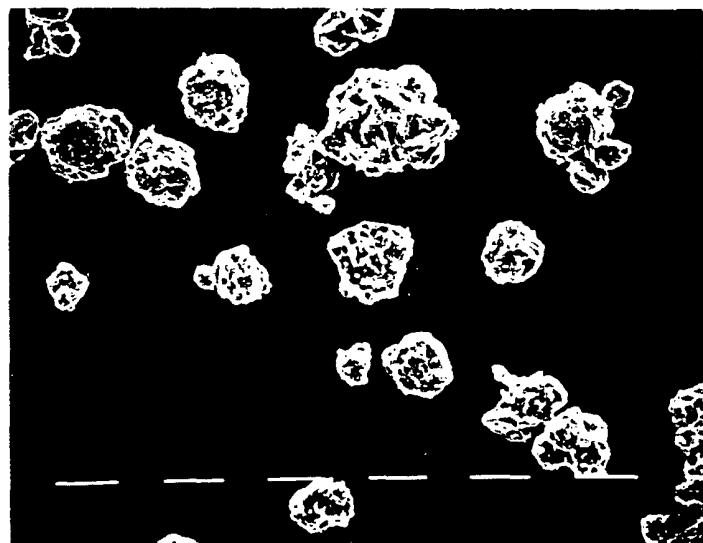
Fig. 9

SEM photograph (30,000 magnications) of the complex oxide
obtained in Example 6
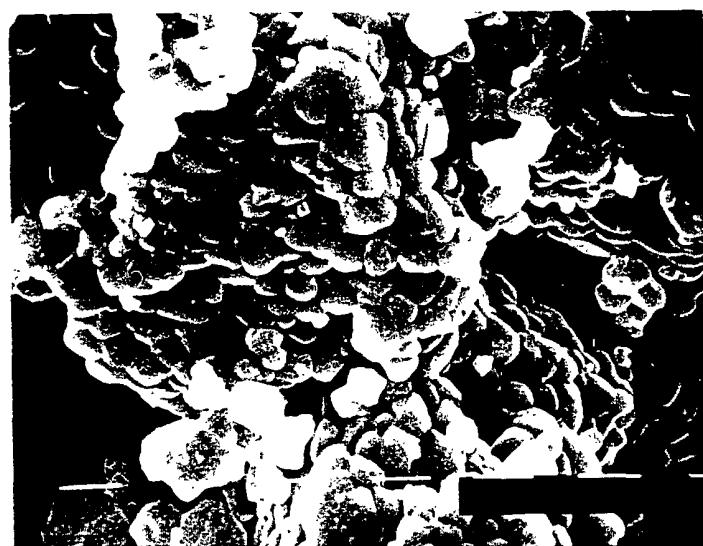
Fig. 10

Particle size distribution of the complex oxide
obtained in Example 6
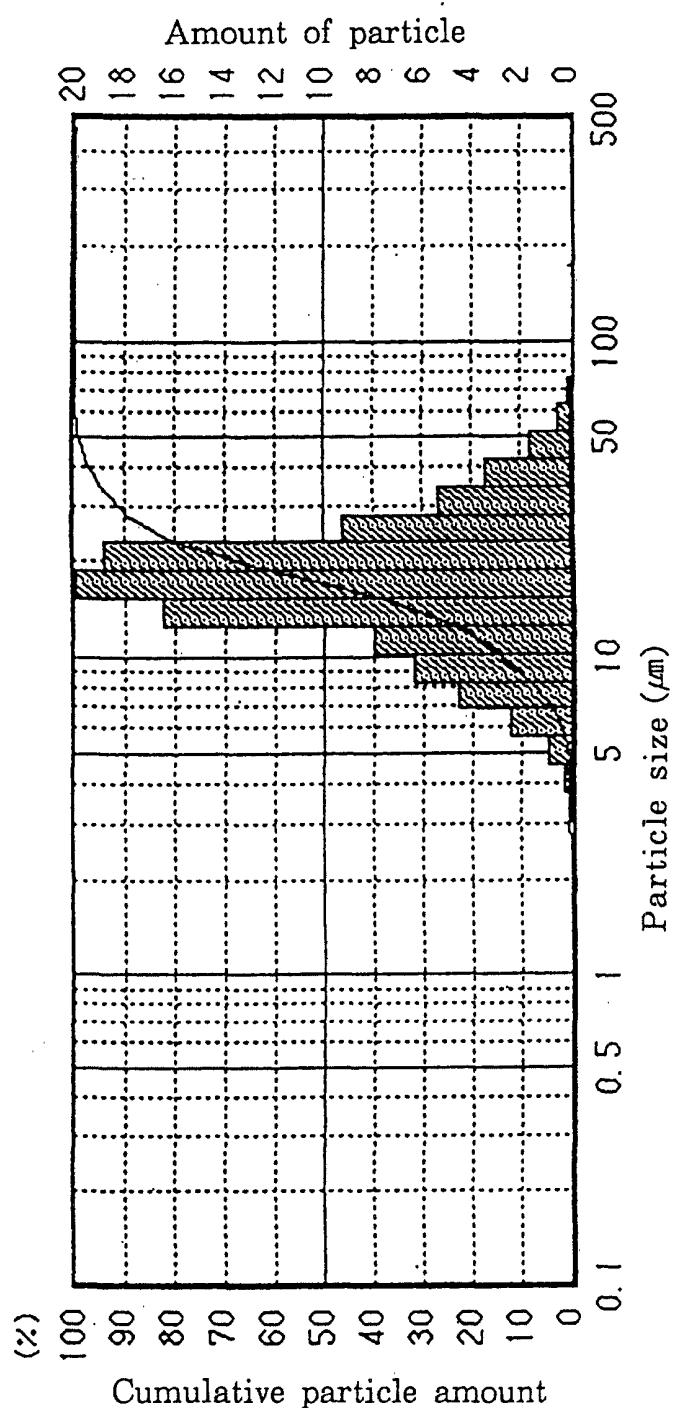
Fig. 11

XRD of the complex oxide obtained in Example 9
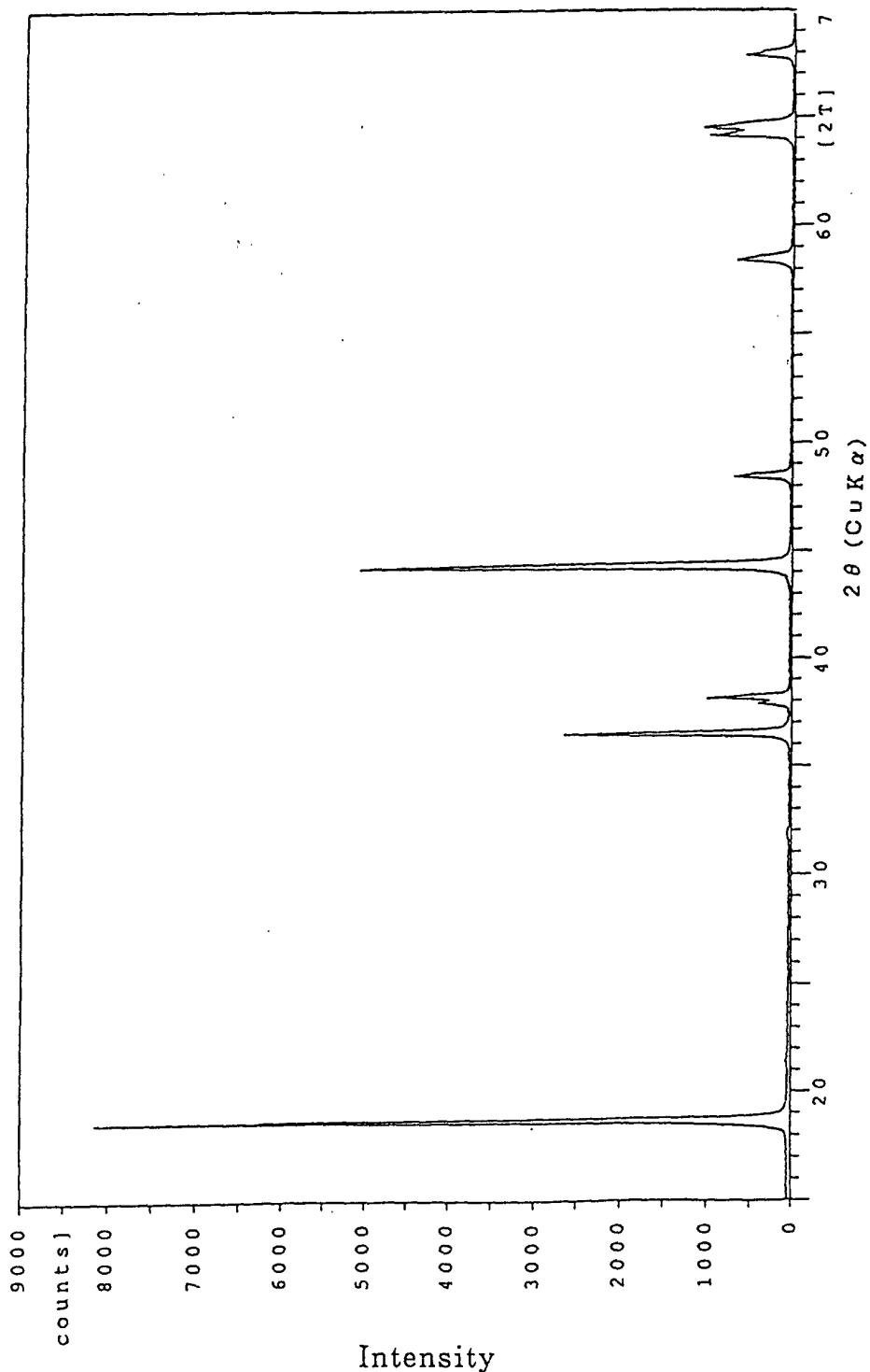
Fig. 12

SEM photograph (10,000 magnications) of the complex oxide
obtained in Example 9
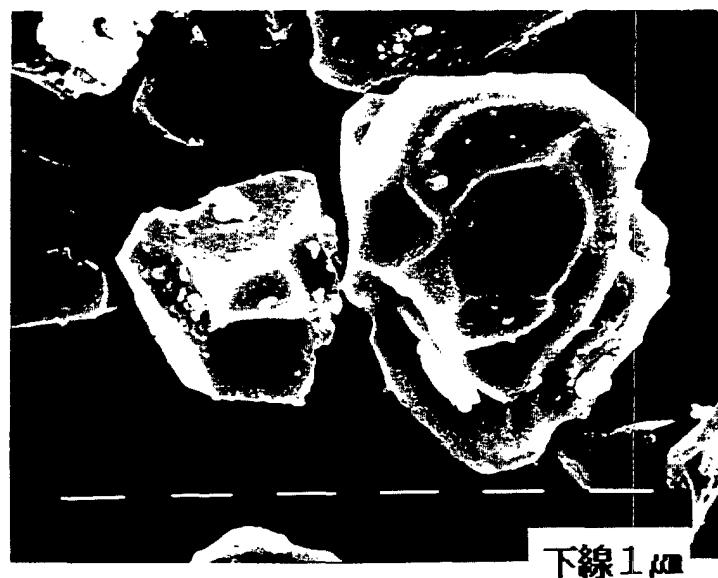
Fig. 13

XRD of the complex oxide obtained in Example 10
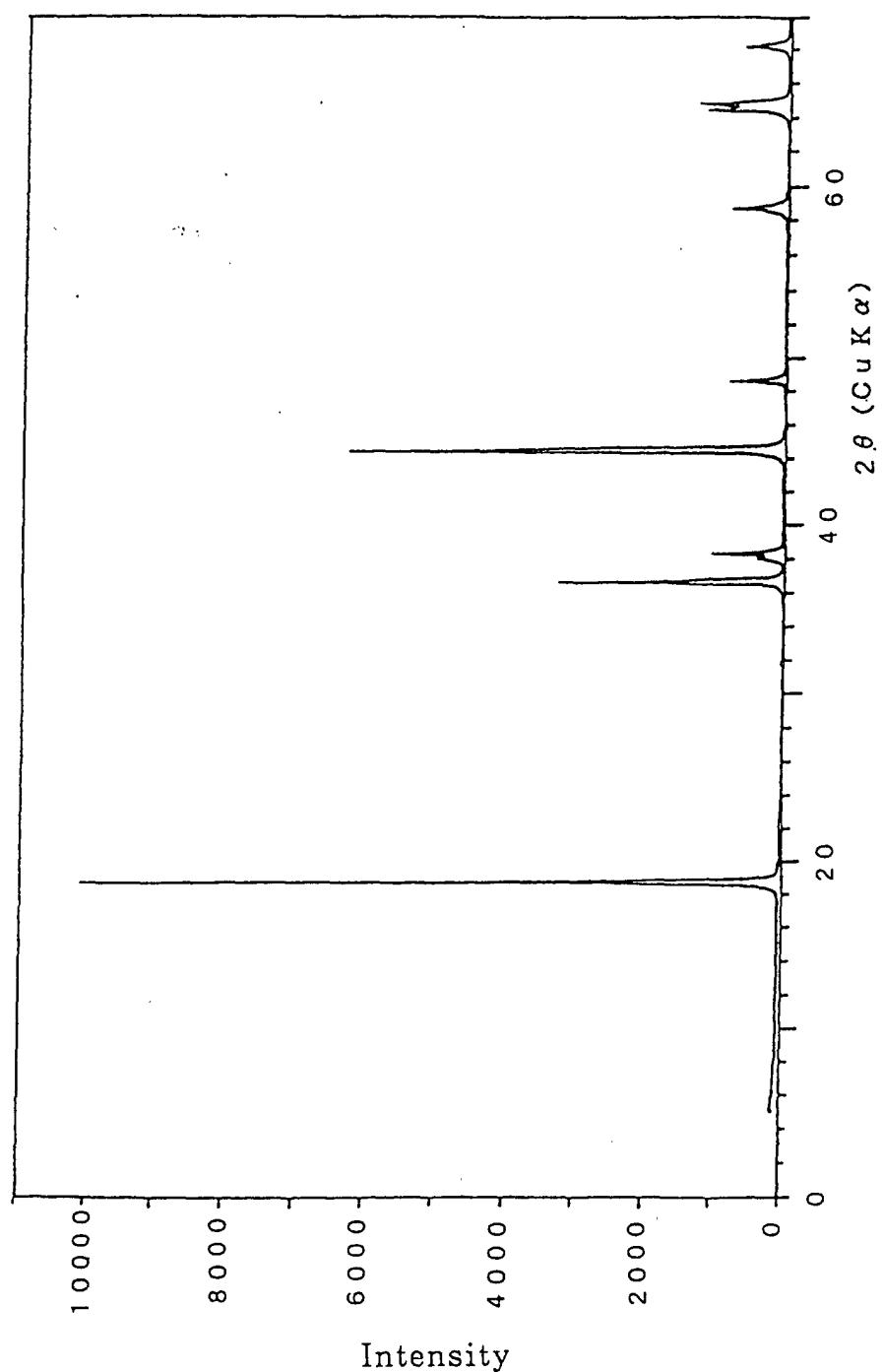
Fig. 14

SEM photograph (30,000 magnications) of the complex oxide obtained in Example 10
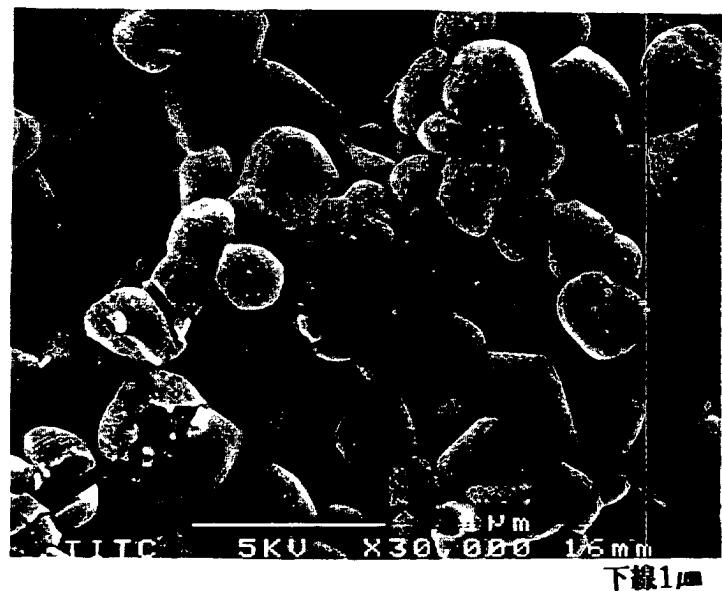
下線1μ

Fig. 15

Particle size distribution of the complex oxide
obtained in Example 10

Amount of particle

Cumulative particle amount
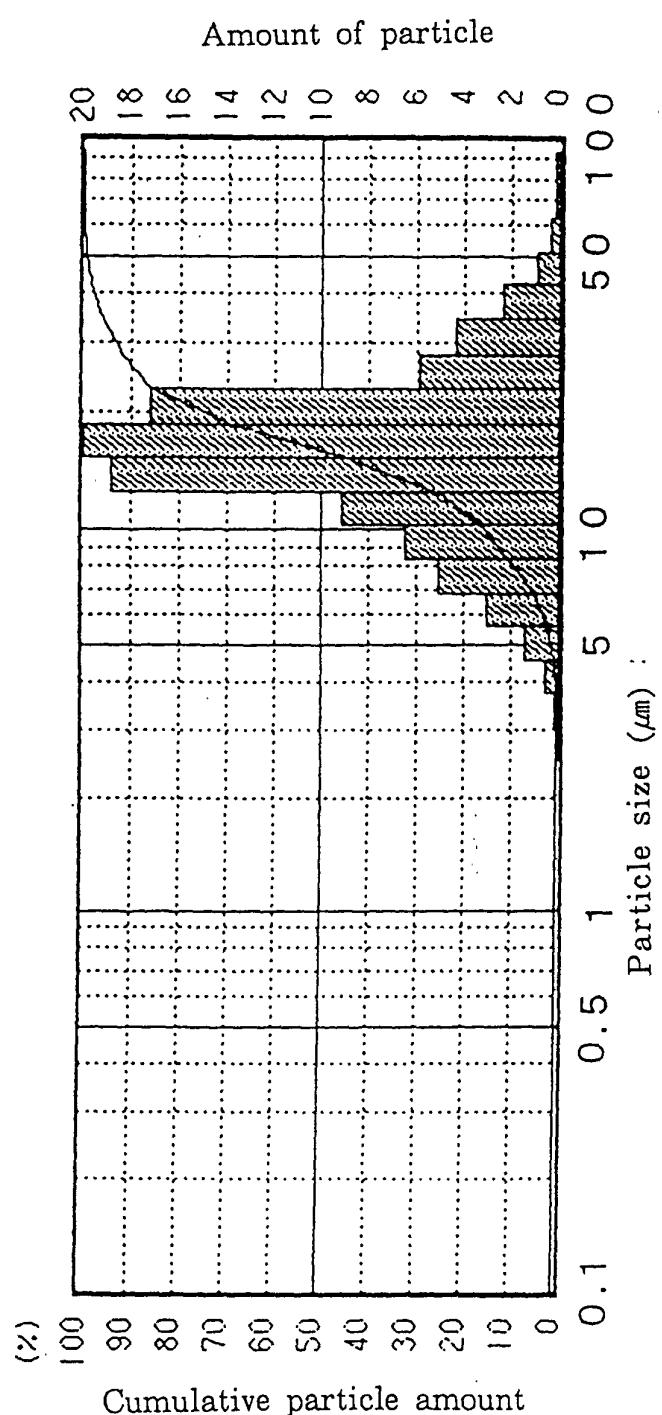
Fig. 16

XRD of the complex oxide obtained in Example 13
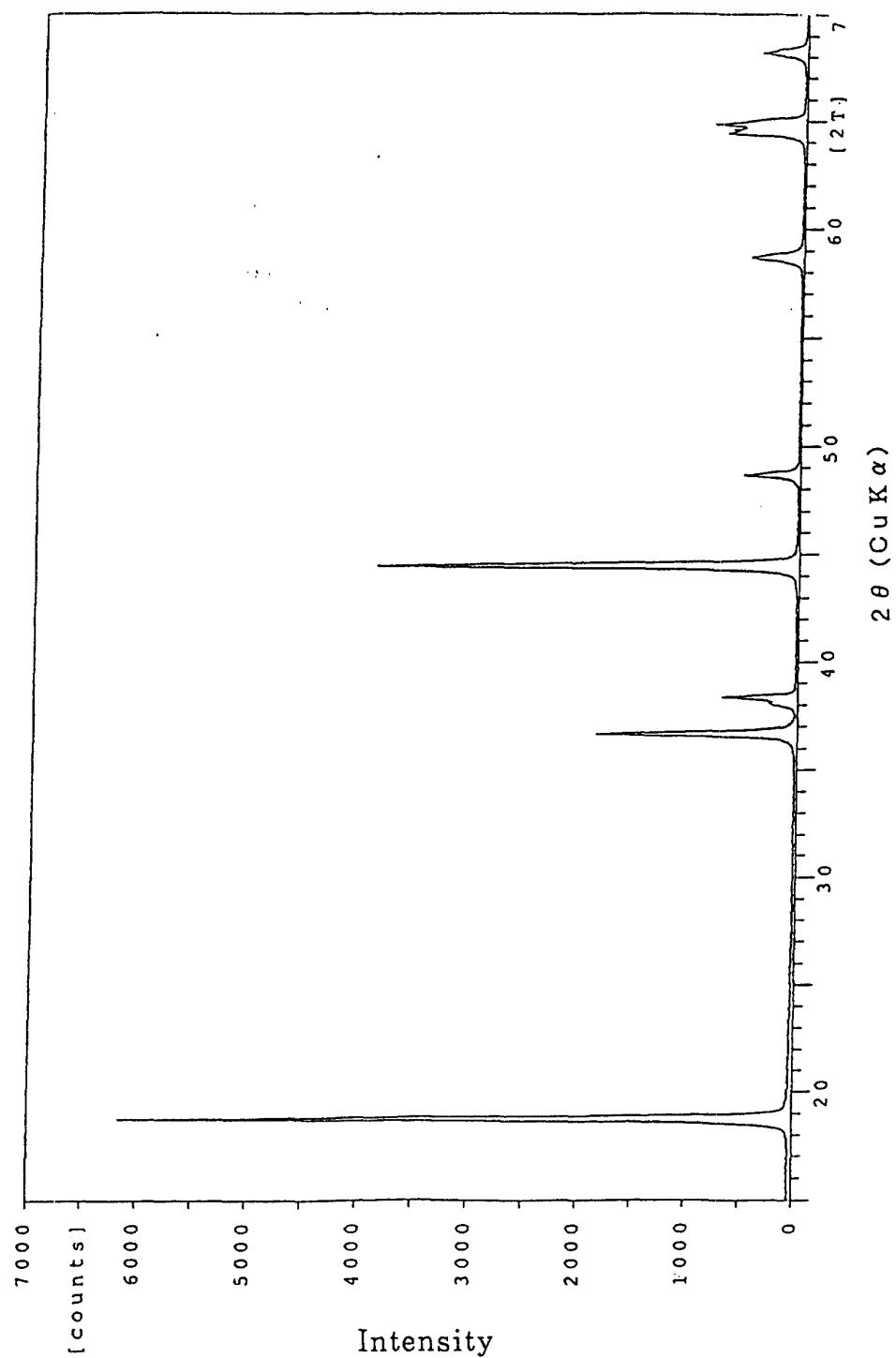
Fig. 17

SEM photograph (10,000 magnications) of the complex oxide
obtained in Example 13

Fig. 18

XRD of the complex oxide obtained in Example 14
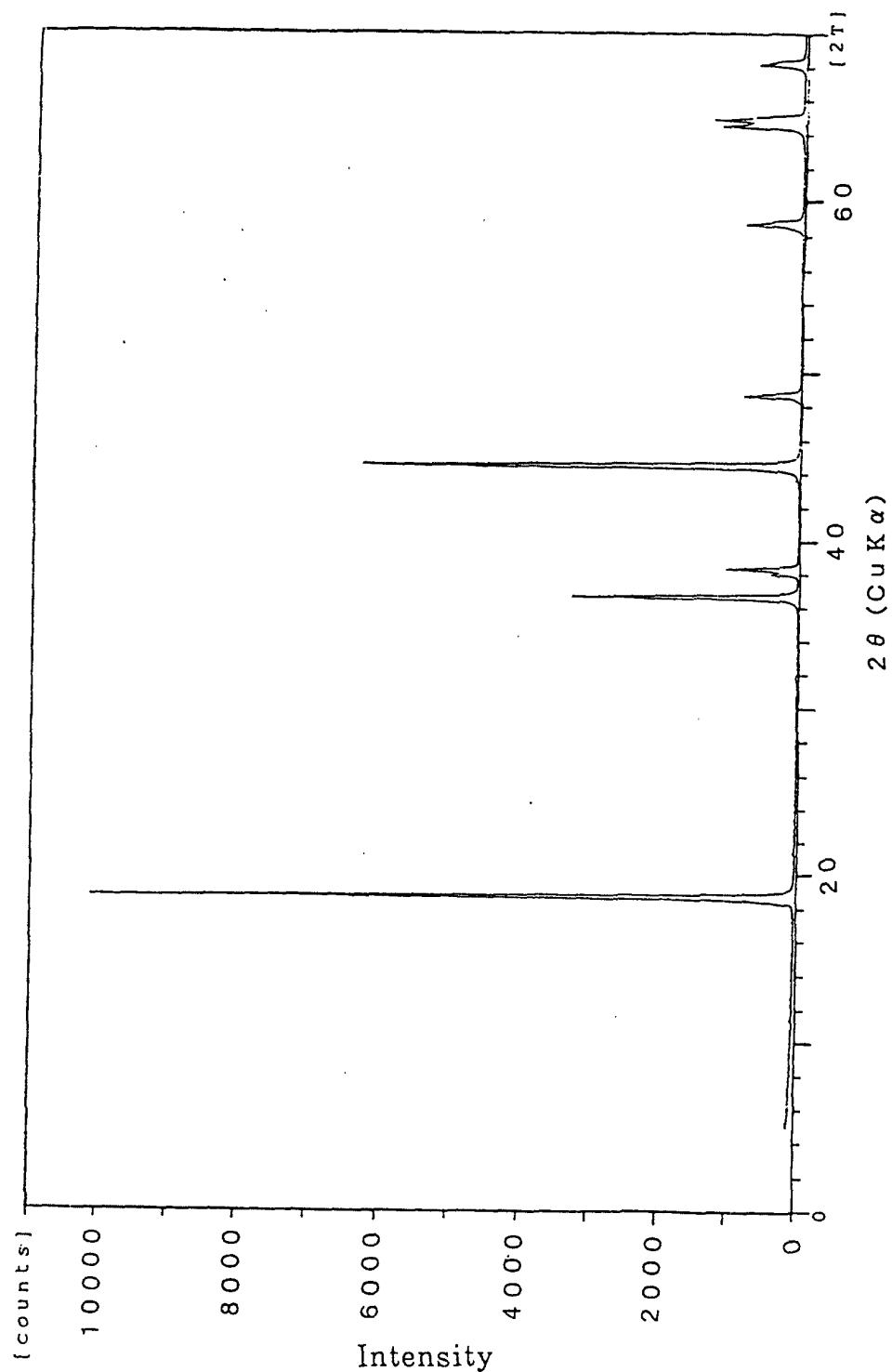
Fig. 19

SEM photograph (150 magnications) of the complex oxide obtained in Example 14

下線１０ μm
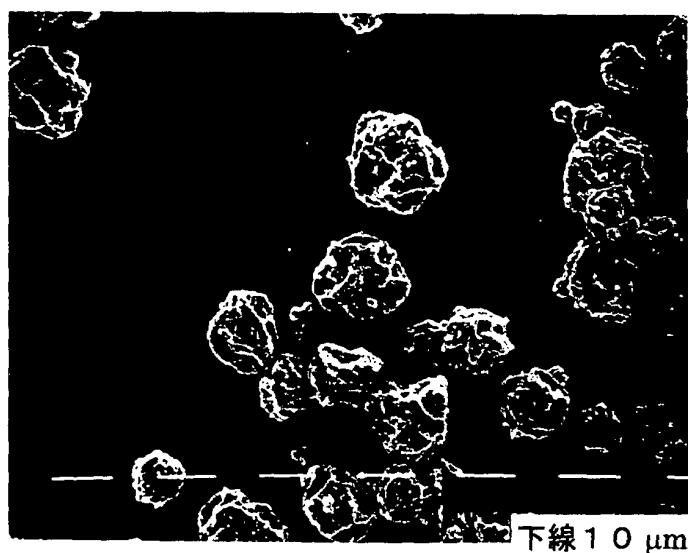
Fig. 20

SEM photograph (10,000 magnications) of the complex oxide obtained in Example 14

下線1 μm
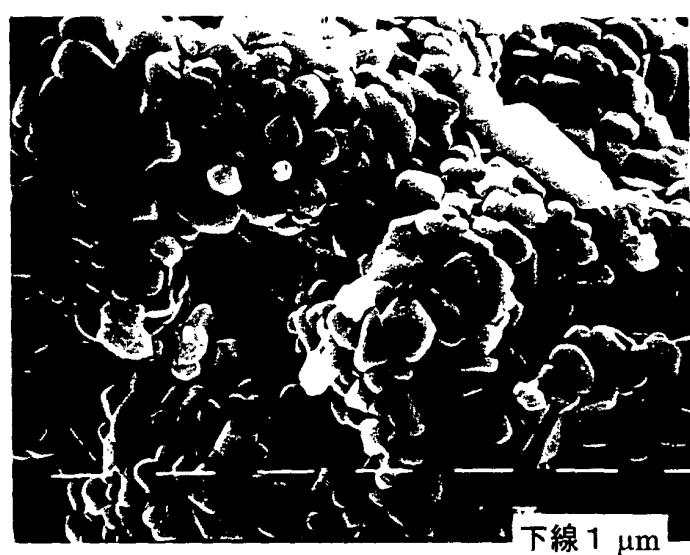
Fig. 21

Particle size distribution of the complex oxide
obtained in Example 14
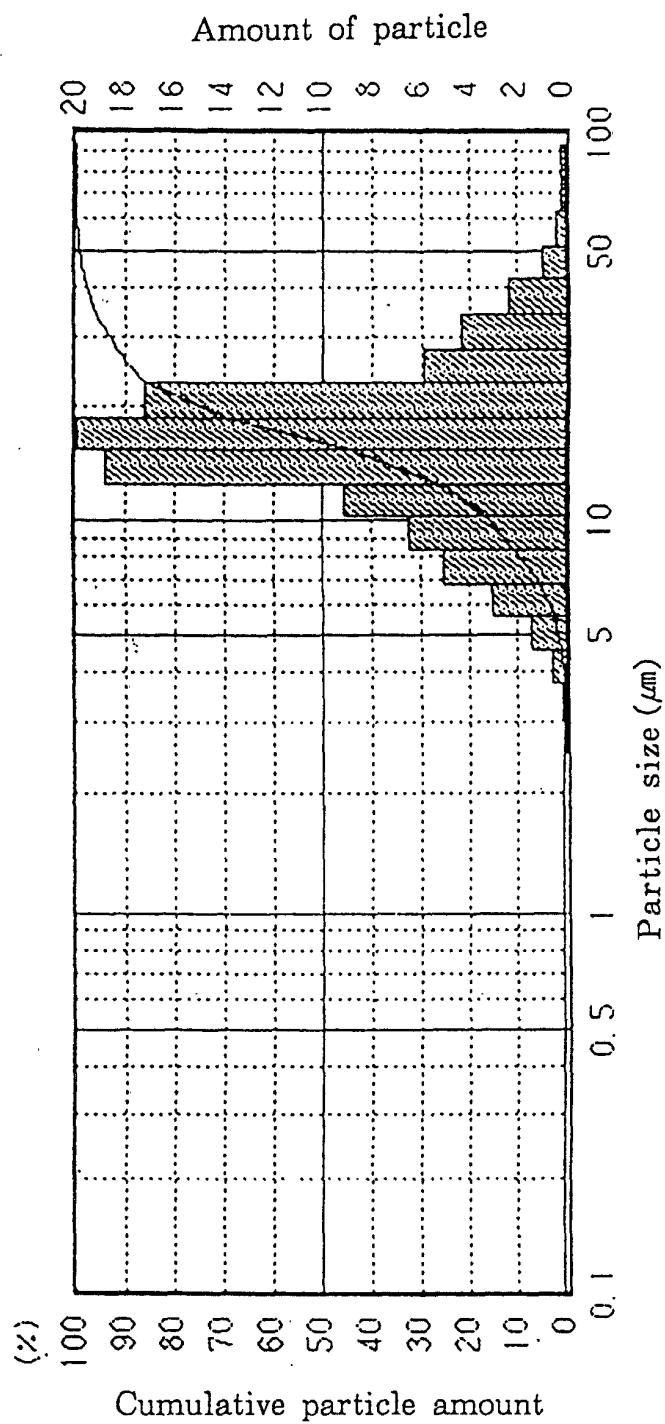
Fig. 22

XRD of the complex oxide obtained in Example 16
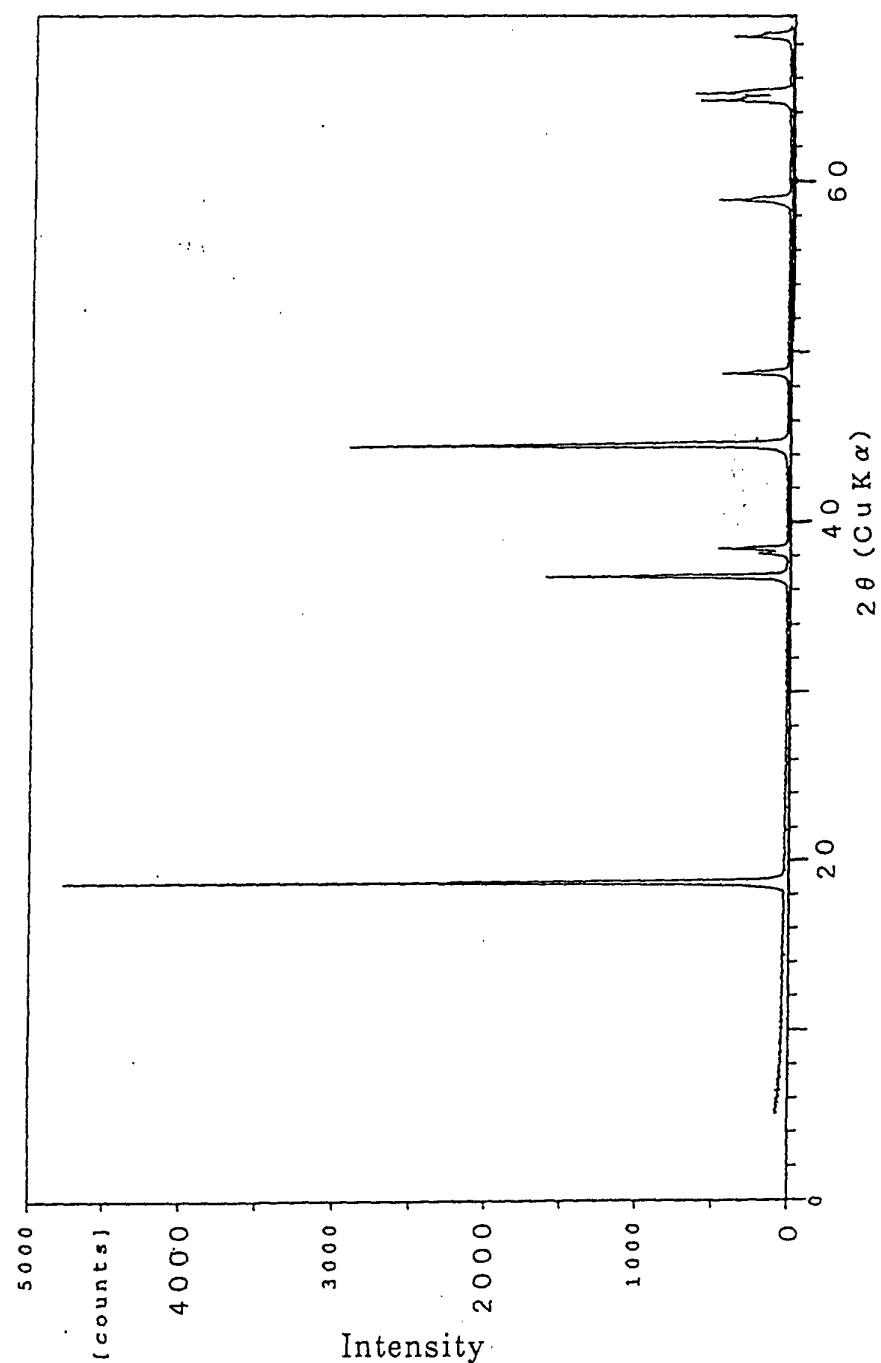
Fig. 23

SEM photograph (1,000 magnications) of the complex oxide obtained in Example 16

下線10µm
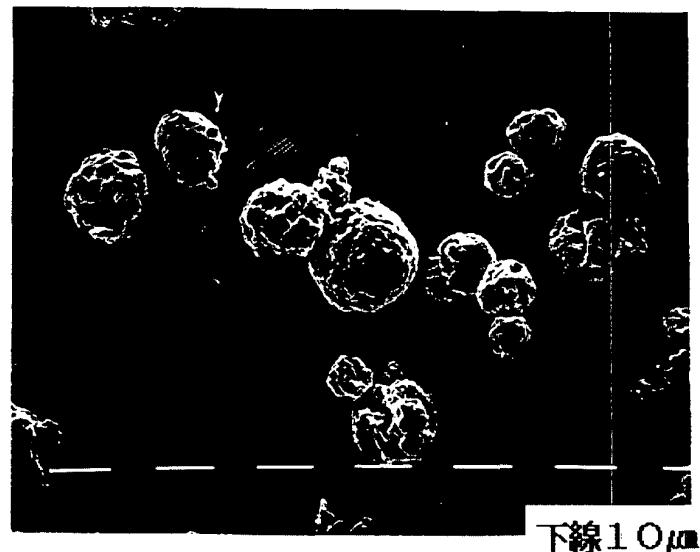
Fig. 24

SEM photograph (10,000 magnications) of the complex oxide obtained in Example 16

下線1µm
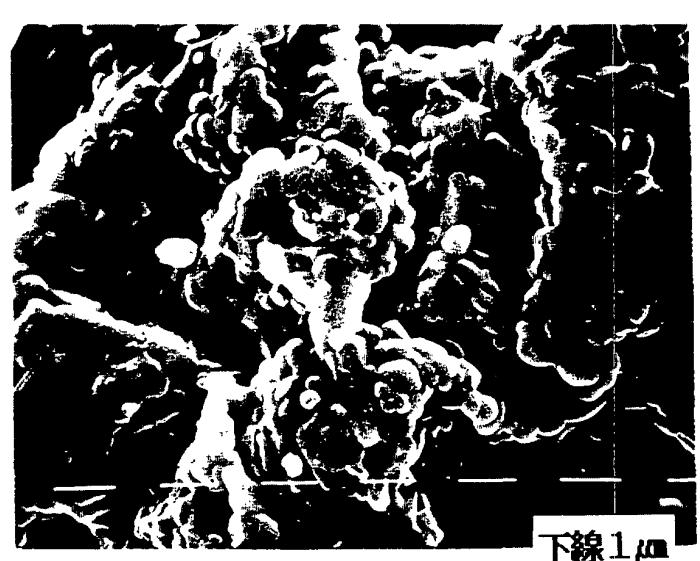
Fig. 25

Particle size distribution of the complex oxide
obtained in Example 16
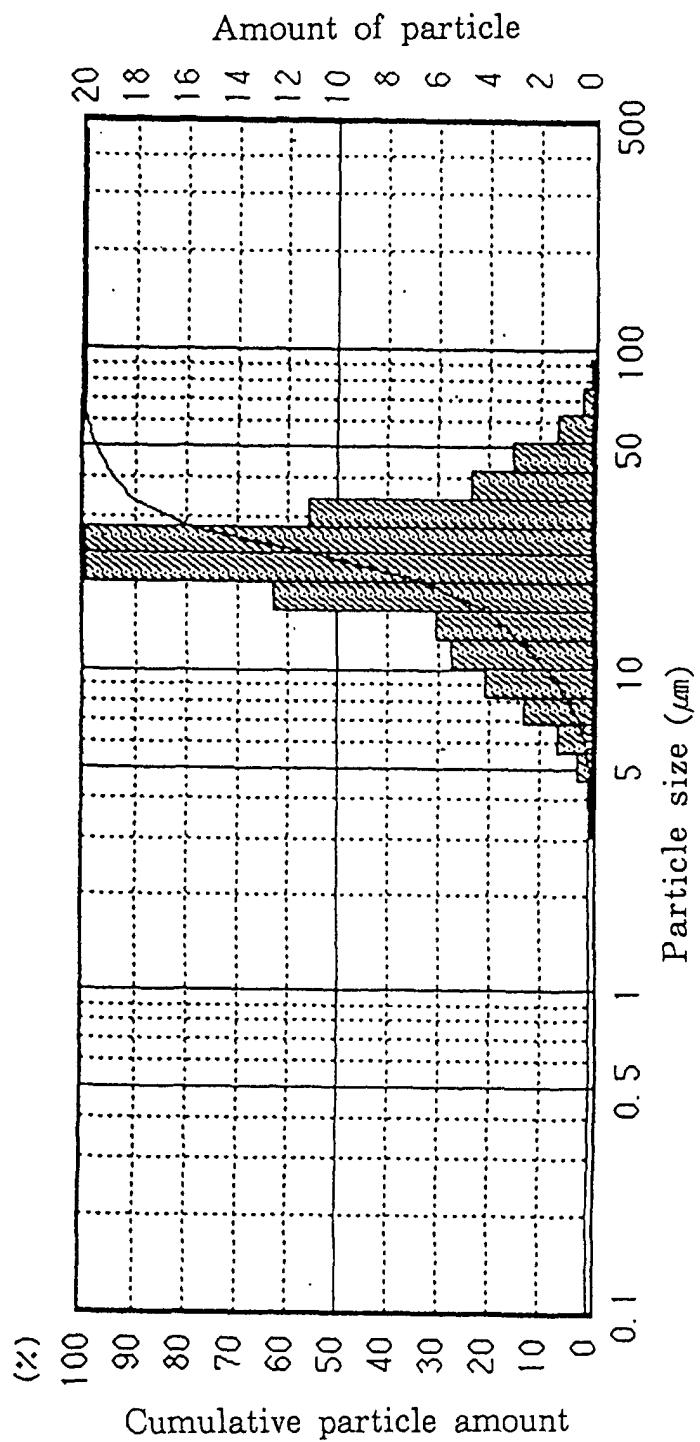
Fig. 26

XRD of the complex oxide obtained in Example 19
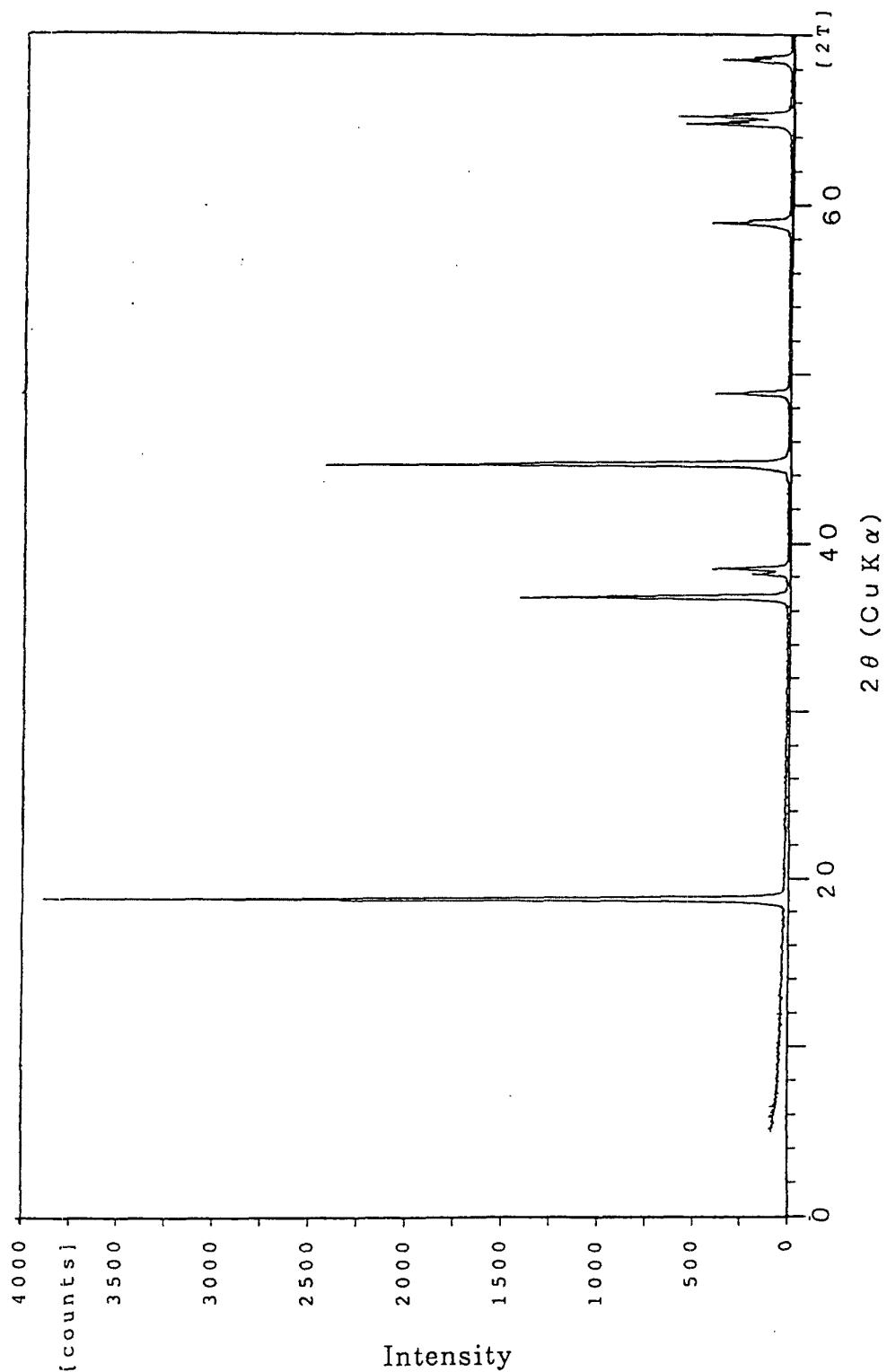
Fig. 27

SEM photograph (10,000 magnications) of the complex oxide obtained in Example 19

下線1 μm
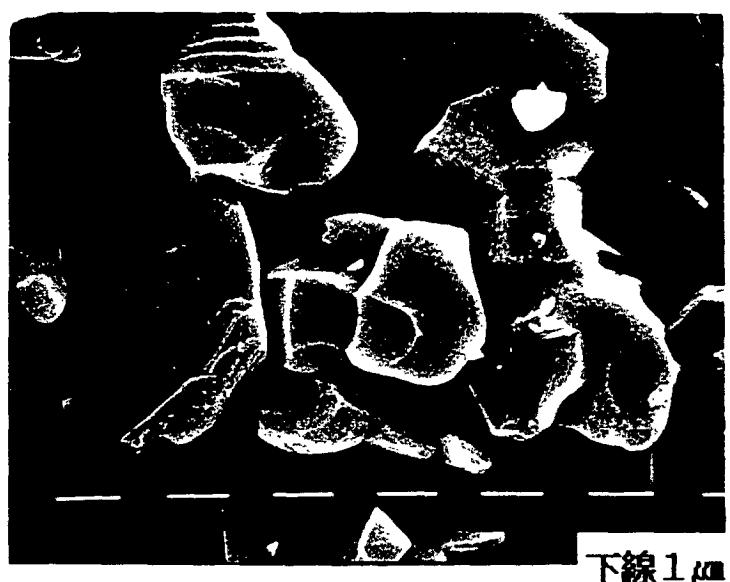
Fig. 28

XRD of the complex oxide obtained in Example 21
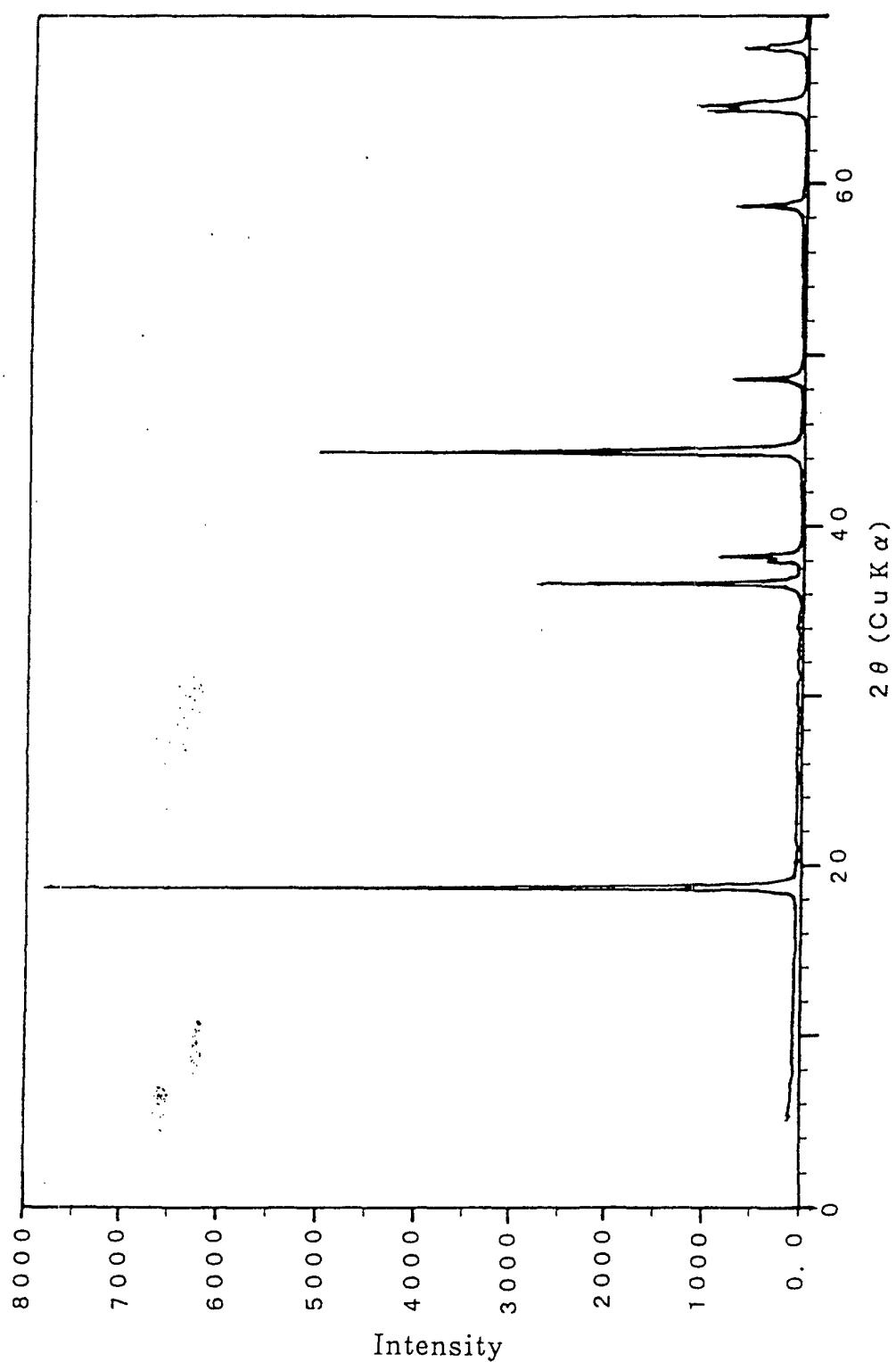
Fig. 29

SEM photograph (50 magnications) of the complex oxide obtained in Example 21
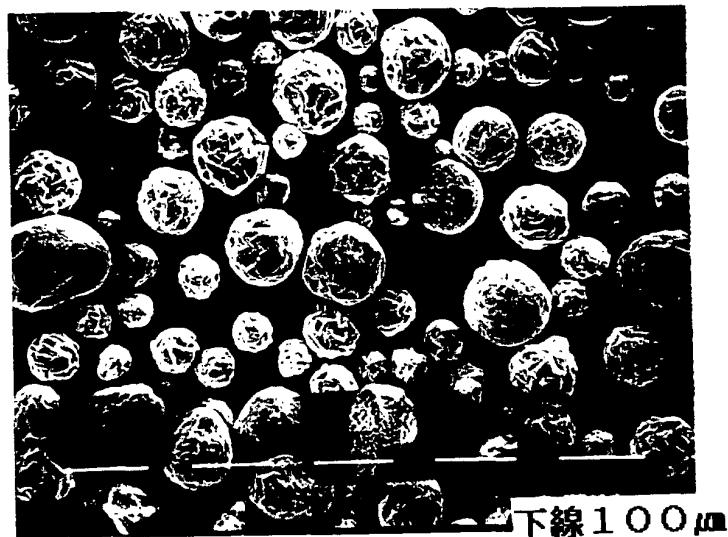
Fig. 30

SEM photograph (30,000 magnications) of the complex oxide obtained in Example 21

Fig. 31

Particle size distribution of the complex oxide
obtained in Example 21
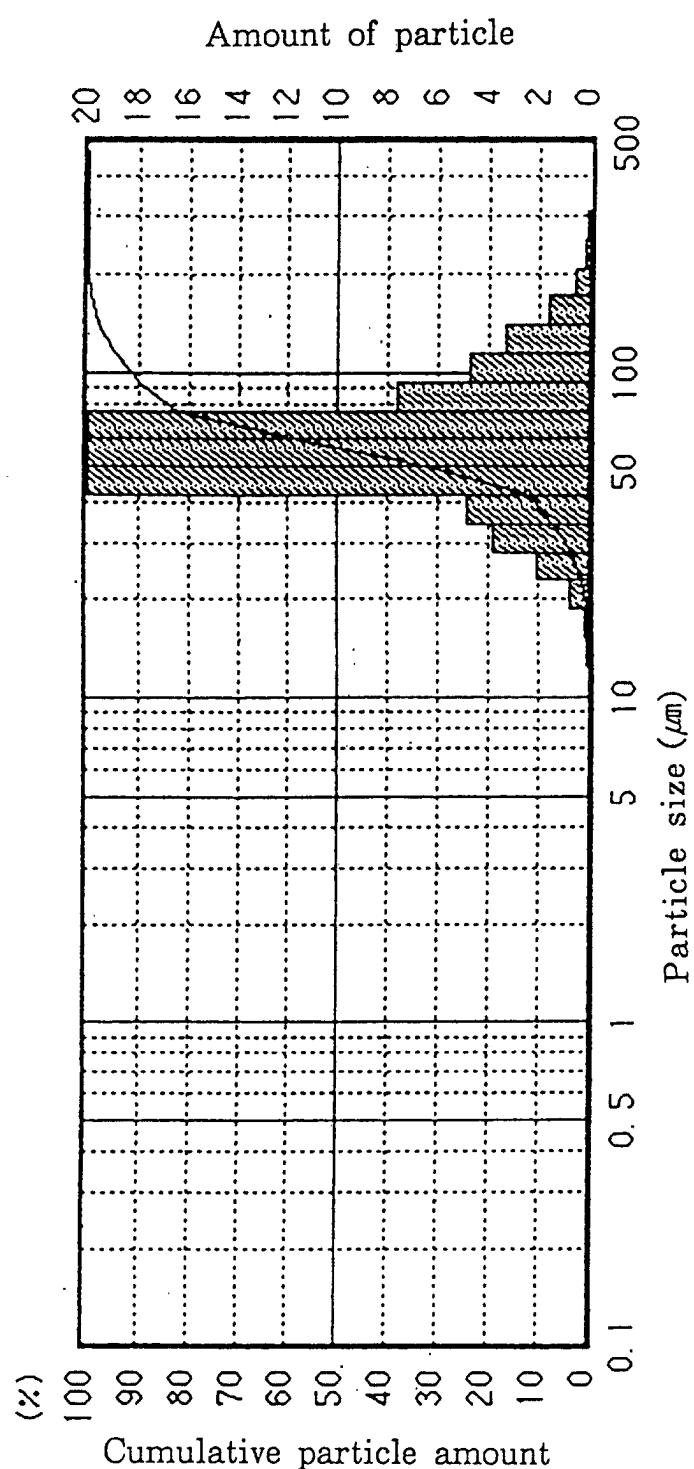
Fig. 32

XRD of the complex oxide obtained in Comparative Example 1
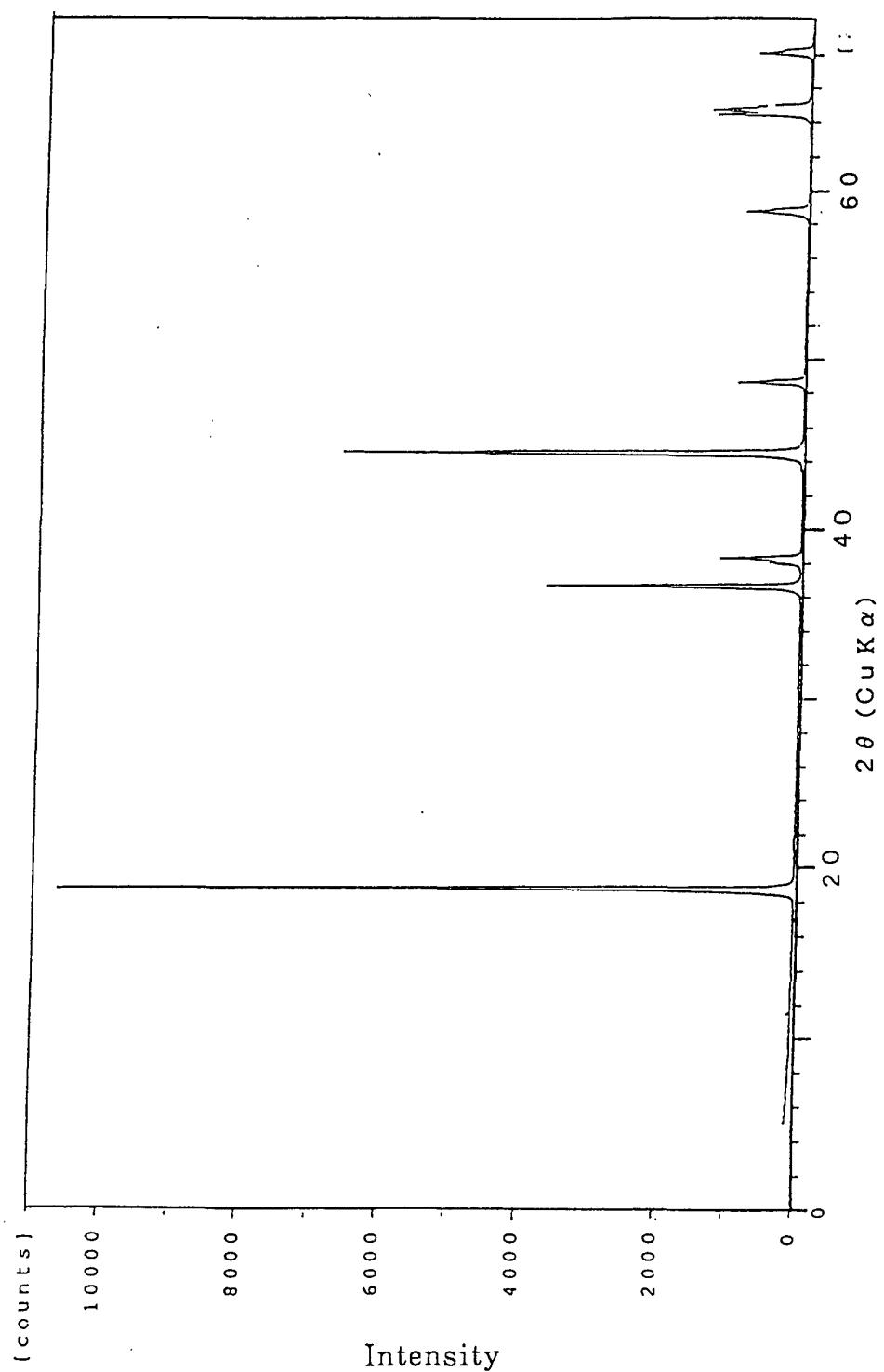
Fig. 33

SEM photograph (1,000 magnications) of the complex oxide
obtained in Comparative Example 1

下線１０ μm
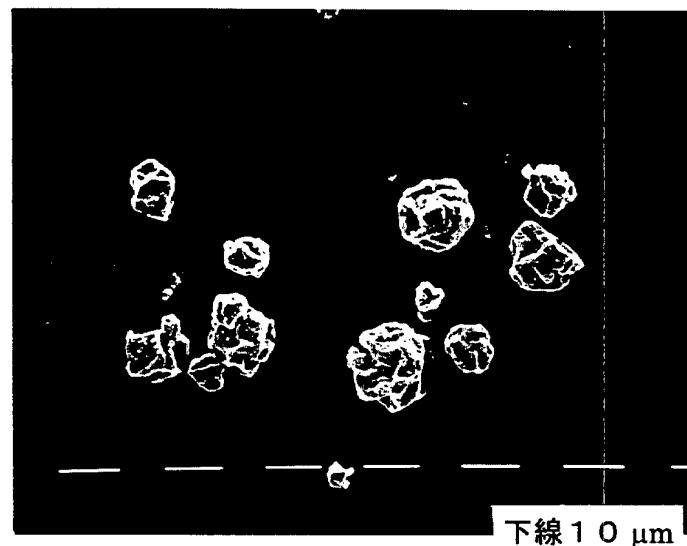
Fig. 34

SEM photograph (10,000 magnications) of the complex oxide
obtained in Comparative Example 1

下線１ μm
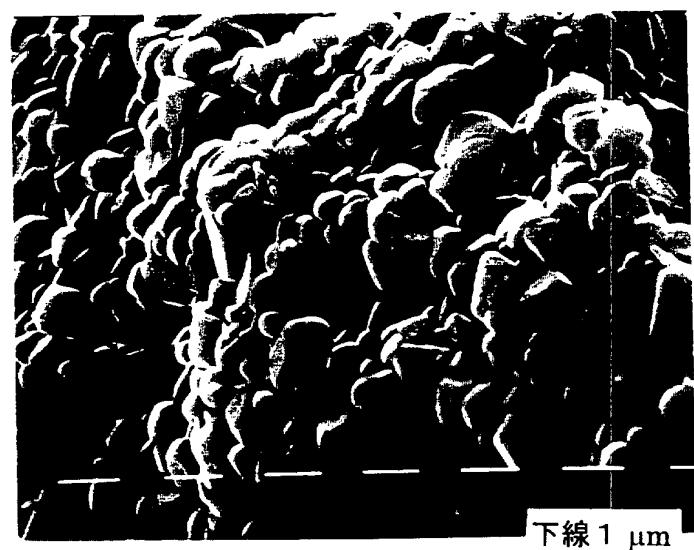
Fig. 35

Particle size distribution of the complex oxide
obtained in Comparative Example 1
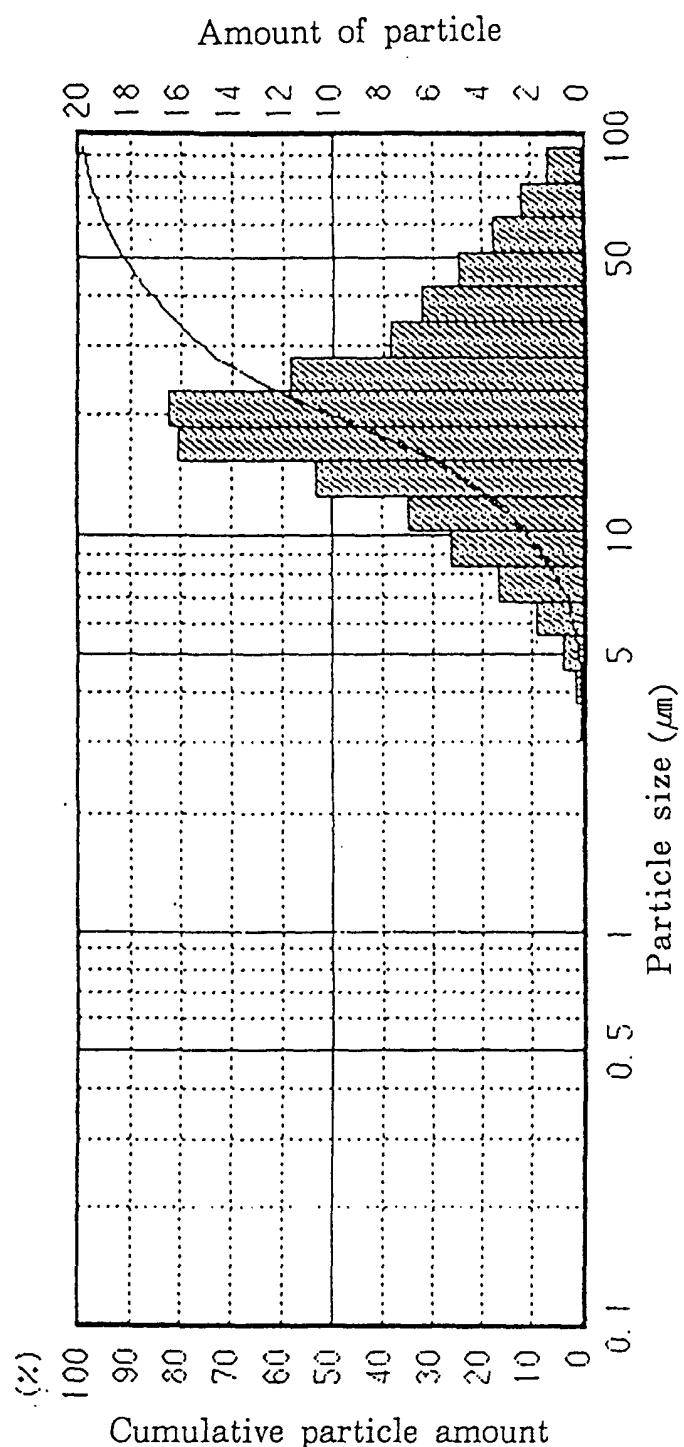
Fig. 36

XRD of the complex oxide obtained in Comparative Example 5
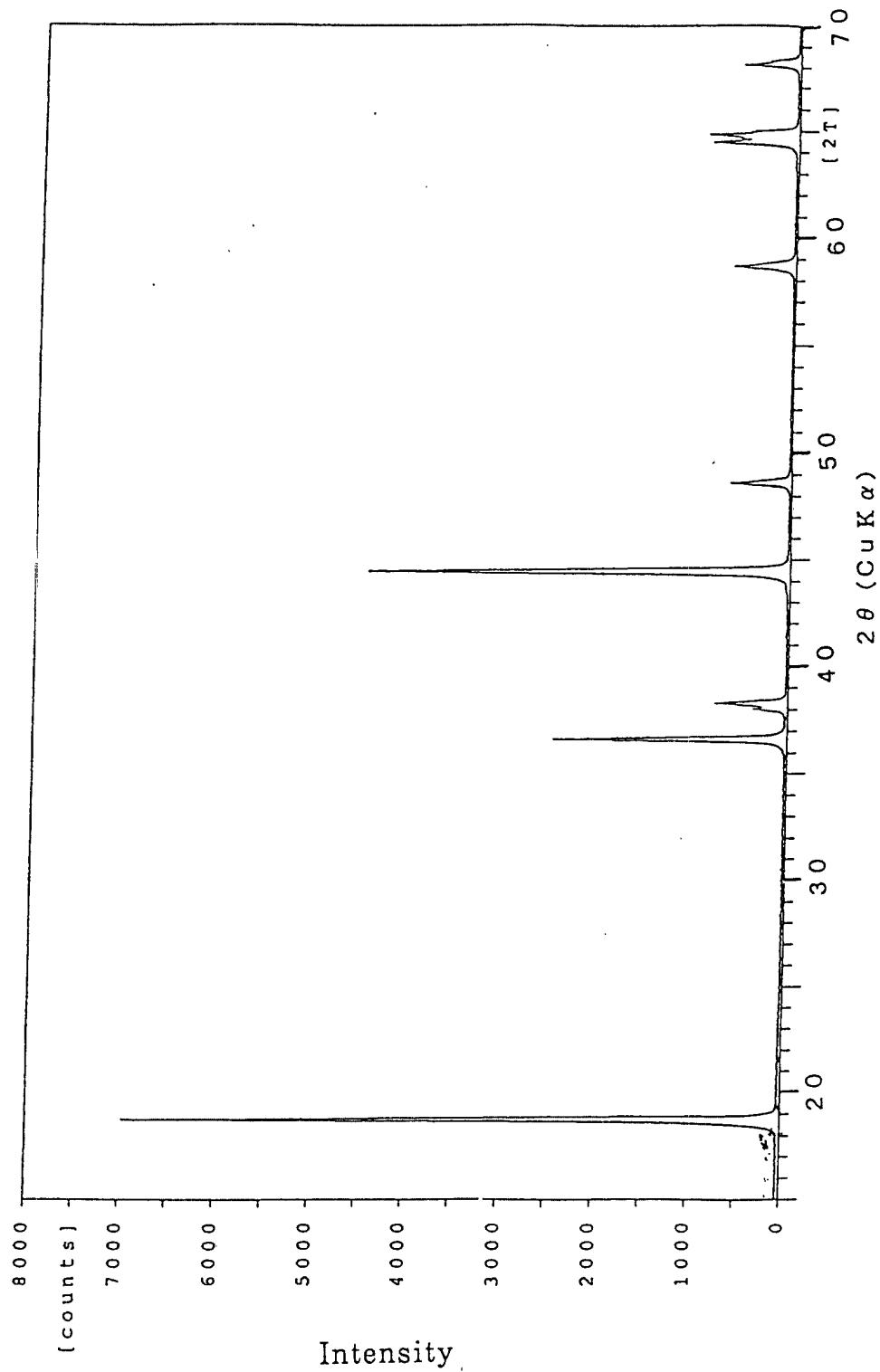
Fig. 37

SEM photograph (3,500 magnications) of the complex oxide obtained in Comparative Example 5
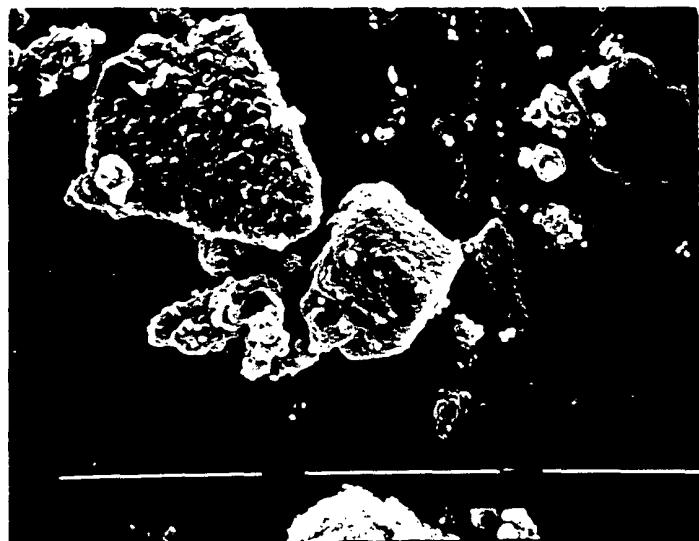
Fig. 38

SEM photograph (10,000 magnications) of the complex oxide obtained in Comparative Example 5
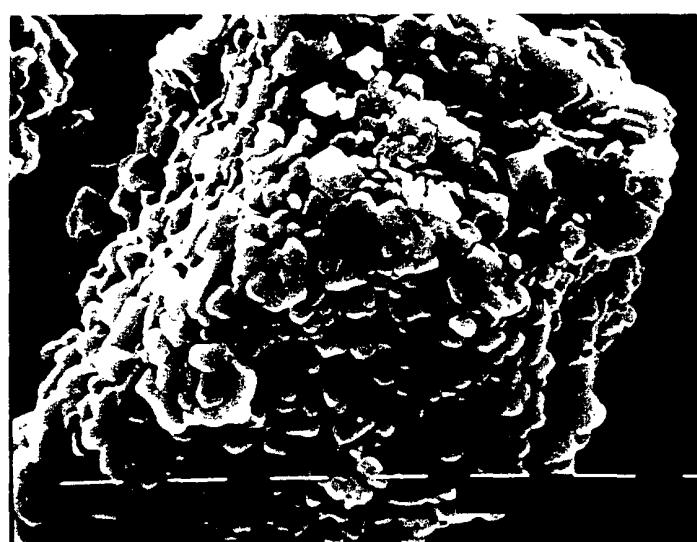
Fig. 39

XRD of the complex oxide obtained in Comparative Example 15

Fig. 40

SEM photograph (20,000 magnications) of the complex oxide obtained in Comparative Example 15